



Measurement of the solidus and liquidus in the U-Zr system by the spot-technique



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ABSTRACT

The solidus and the liquidus of U-Zr system were determined using the “spot-technique” over the entire composition range. The experimental facility was fabricated in-house and installed in a glove box for investigating solid to liquid phase transitions in radioactive alloys. This equipment is capable of operating in the temperature range 1273–2273 K. U-Zr alloys of desired composition were prepared by arc melting the constituent elements in required proportion. These alloys were heated by radiofrequency (RF) induction under vacuum and the change in their optical reflectivity was monitored. Chemical analyses of U-Zr alloys indicate that the uncertainty in the composition is ± 1.3 at.% Zr (max.). The accuracy of the temperature measurement was ascertained by measuring the melting points of high purity Au, Cu, Ni and Zr. The measured values of the melting points were accurate within ± 3 K. This is the first time that the solidus and the liquidus of U-Zr system were determined by using a single experimental technique over the entire composition range.

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1. Introduction

Ternary U-Pu-Zr alloys are being considered as candidate fuels for the Indian Fast Reactors [1–4] with a Zr content of 6 wt% and a Pu content ranging from 19 to 22 wt%. These alloys have been used as a fuel in reactors worldwide and have significant advantages over the conventional mixed U, Pu oxide fuel [5–8]. A complete thermodynamic and constitutional characterization of the ternary system and all its limiting binaries are useful in both the fabrication as well as in understanding the in-pile behavior of these fuels. Amongst the three limiting binaries U-Zr is the most important. There are several studies focusing on solid state phase transformations, heat capacities as well as the enthalpies of formation of this system [9–22]. The solidus and the liquidus of some compositions were experimentally determined by metallography and optical pyrometry [9], vapor pressure studies [12–14], differential thermal analysis (DTA) [10,22], and differential scanning calorimetry (DSC) [15]. However, solidus and liquidus have not been measured over the entire composition range and there are still some uncertainties in the experimental data. Recent work by

Westphal et al. [23] mentions that the liquidus region is not as well defined as other portions of the U-Zr phase diagram. Ahn et al. [16] report that more information on a reliable phase diagram and relevant thermophysical properties are essential for developing a fuel performance code. Apart from these experimental studies the U-Zr has been modeled using the Calphad method by many authors [11,24–32]. From the above discussions it is evident that the experimental data on the solidus and the liquidus of a few selected compositions are only available and these measurements do have uncertainties. Hence in the present study, we have re-determined the solidus and the liquidus of the U-Zr system over the entire composition range for the first time by using a custom-built equipment that employs the spot technique.

1.1. The spot technique

The spot technique is a relatively simpler technique devised by Ackermann and Raugh [33] for determining solidus and liquidus. It is a convenient method particularly for alloys containing refractory and/or radioactive metals for it is amenable for glove box adaptation. This technique falls under the category of thermo-optometry, wherein the change in the optical reflectivity of the sample upon liquefaction during heating is monitored. In this technique, the

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sample is heated in a Knudsen cell (K-Cell) held under vacuum by radiofrequency (RF) induction. The surface of the sample is monitored through the orifice atop the K-Cell lid by a magnifying device. The temperature is measured from the black body hole at the bottom of the K-Cell by a pyrometer. Upon melting, the liquid formed on the surface of the sample acts as a mirror and reflects the image of the orifice. The appearance of this image (as a single circular dark spot) corresponds to the melting point. In case of alloys, the first appearance of broken irregular dark tiny patches corresponds to the solidus. On further heating, several tiny irregular dark patches appear due to the formation of many droplets. These grow in size with the quantity of the liquid and finally coalesce into a single large dark circular spot at liquidus. Fig. 1 is a schematic representation of the reflections observed on the sample surface at different temperatures. Further details about the technique can be found elsewhere [34–40].

2. Experimental

2.1. Starting materials

High purity Zr (min. 99.5 wt%) in the form of a wire procured from m/s. Advent, USA and reactor grade U (min. 99.9 wt%) from m/s. Atomic Fuels Division, BARC, Mumbai were used for making the alloys. Analytical reagent (AR) grades of HNO_3 , H_2SO_4 and HF from m/s. Merck, Mumbai, were used for the dissolution of the alloys. Xylenol orange of TCI make, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (>99% pure), sodium salt of ethylene diamine tetra acetic acid (EDTA) (>99.5% pure), pyridine (min 99.5% pure), sulphamic acid (99.9% pure), potassium-di-chromate (99%), $\text{o-H}_3\text{PO}_4$ (88% min) and ferrous ammonium sulphate (99% pure) supplied by m/s. Merck, Mumbai, ammonium molybdate (99% pure) from m/s. Fischer, Mumbai, vanadyl sulphate obtained from m/s. BDH Chemicals, Mumbai were used in the chemical assay of U–Zr. All these chemicals were AR grade.

2.2. Preparation of alloys

U–Zr alloys of desired composition were prepared by arc melting appropriate quantities of U and Zr in argon atmosphere at about 1 Pa. Arc melting was carried out in a tri-arc furnace supplied by m/s. Centorr, USA. A thoriated tungsten electrode was used for melting. To ensure the homogeneity of the alloy, the ingot was flipped and melted thrice. The arc melting chamber was evacuated to 1 Pa and flushed with high purity argon (IOLAR – 2 grade; <

4 ppm of O_2 and H_2O ; supplied by m/s. INOX Air Products, Chennai) for atleast six times. Fresh U pieces required for the preparation of the alloys were cleaned by dipping them in dilute HNO_3 , water and acetone in that order. The Zr wire was scrubbed with SiC coated emery (fine grade) and then wiped with acetone.

U–Zr alloys are prone to oxidation during arc melting. In order to limit this, a freshly cleaned piece of U was used as getter for oxygen prior to the melting of alloy. This reduced the oxidation significantly. The weight of the alloy after melting was compared with the sum of weights of U and Zr before arc melting. Alloys that did not show any appreciable change in weight were only used for measuring the solidus and liquidus.

2.3. Crucible fabrication

Yttria crucibles required for holding the alloy during the solidus and liquidus measurements were fabricated in-house by cold compaction at a pressure of 120 MPa without any binder. A biaxial hydraulic press supplied by m/s. Bemco Hydraulics Ltd, India was used for the compaction with tungsten carbide lined die and High Carbon – High Chromium (HC-HCr) plungers. The green crucibles (typically outer diameter $\times$ inner diameter $\times$ thickness = $9 \times 7 \times 8$ mm) were sintered in air for 4 h at 1673 K with a heating and cooling rate of 5 K min^{-1} . A furnace equipped with molybdenum di-silicide heating elements was used for the sintering.

2.4. Solidus and liquidus measurements

The experimental setup used in the present study is shown in Fig. 2 (a), while Fig. 2 (b) shows the schematic of the vacuum heating chamber. The assembly of a typical K-Cell and the crucible is shown in Fig. 3. In a typical experiment the sample (about 400 mg) kept in an yttria crucible enclosed in a K-Cell, was heated by radio-frequency (RF) induction under vacuum (10^{-4} Pa). The temperature was measured by a two-colour pyrometer (M770S of m/s. Mikron make, USA) that was focused onto the black body hole provided at the bottom of the K-cell. The surface of the sample was viewed by a long distance microscope (Model: QM1, m/s. Questar Inc., USA) through the orifice (1 mm diameter) in the lid of the K-cell. Changes in the optical reflectivity of the sample (acquired by the CCD camera at the rear of the long distance microscope) were viewed on the display screen. The corresponding video was also recorded through suitable software. The temperatures corroborating to the changes in the optical reflectivity of the sample were noted as solidus or liquidus.

Supplementary video related to this article can be found at <http://dx.doi.org/10.1016/j.jallcom.2016.07.252>.

The following heating routine was employed during the experiments; i) fast heating to a temperature about 50 K below the solidus, ii) moderate heating at 5 K min^{-1} to a temperature that is 15 K below the solidus, and iii) slow heating around 1 K min^{-1} until the sample melts. At the end of step (i) and (ii), the induction heater was maintained at a given power for sufficiently long duration (typically 600 s) in order to ensure the attainment of thermal equilibrium within the K-Cell.

2.5. Temperature calibration

Temperature calibration of the equipment was done by measuring the melting points of high pure metals viz., Au, Cu, Ni, and Zr. The procedure followed was similar to that described in Section 2.4. Graphite/yttria crucibles were used for these measurements. Each measurement was repeated for a minimum of 5 times and the average of the values is reported.

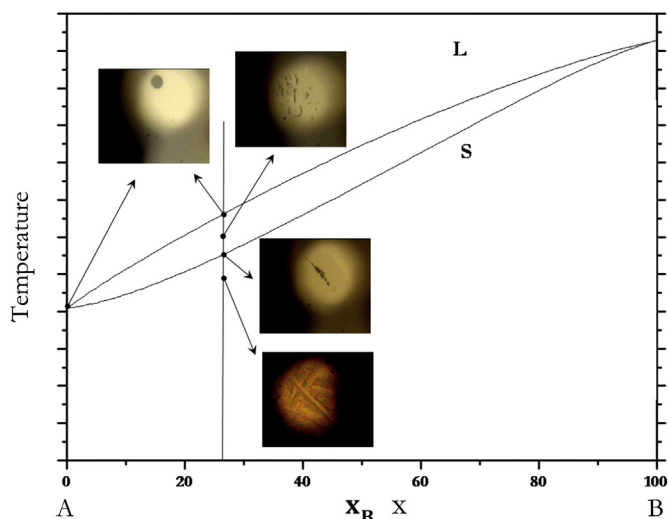


Fig. 1. Schematic of the reflections observed on the sample surface with temperature.

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