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Release of gases from uranium metal at high temperatures

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Abstract

Depending on the ambient environmental conditions, different gaseous species could get entrapped in uranium metal ingots or pellets. On heating, melting or vapourising uranium metal, these get released and depending on the composition, may cause detrimental effects either within the metal matrix itself or on the surrounding materials/environment. For instance, these gases may affect the performance of the uranium metal, which is used as fuel in the heavy water moderated research reactors, CIRUS and DHRUVA. Hence, detailed investigations have been carried out on the release of gases over a temperature range 875–1500 K employing hot vacuum extraction technique, in specimen uranium pellets made from uranium rods/ingots. Employing an on-line quadrupole mass spectrometer, the analysis of released gases was carried out. The isobaric interference between carbon monoxide and nitrogen at $m/e = 28$ in the mass spectrometric analysis has been resolved by considering their fragmentation patterns. Since no standards are available to evaluate the results, only the reproducibility is tested. The precision (relative standard deviation at 3σ level) of the method is ±5%. The minimum detectable gas content employing the method is 5.00×10^{-09} m^3. About 4×10^{-04} m^3/kg of gas is released from uranium pellets, with hydrogen as the main constituent. The gas content increases with storage in air.

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1. Introduction

Uranium is an important nuclear fuel material. In the earliest reactors, natural uranium metal was used as the fuel and aluminum as clad. These reactors were designed to produce plutonium. Aluminum was chosen as clad due to its low thermal neutron absorption cross-section and high corrosion resistance. However, due to low melting temperature, it was not used in power reactors. To overcome the problems encountered with aluminum, Mg–Al and Mg–Al–Zr alloys were chosen. Uranium (natural and depleted) is used as fuel in the gas cooled reactors, gas cooled fast reactors and lead cooled reactors. The gas cooled fast reactors with helium as coolant and liquid metal (Pb or Pb–Bi) cooled reactors are suitable both for power generation and for thermochemical hydrogen production. Uranium in alloy form is also employed as fuel in nuclear submarines. The accelerator driven reactor systems also use uranium as fuel. In light water reactors (LWR), enriched uranium as UO_2 is used.

Uranium metal is produced by different methodologies [1–4]. Based on the expected burn-up aimed at, the fissile atom density has to be increased. This is generally achieved by employing enriched uranium. There are several methods available for the enrichment of uranium. LASER technique is one of the most sensitive and economical methodologies. However, it is in the developing stages in several countries. LASER method employs either molecular or atomic approach, the later judged as better one. In Atomic Vapour Laser Isotope Separation (AVLIS) technique, uranium vapour, produced by heating uranium metal to ~2500 K, is subjected to selective ionisation followed by magnetic

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sector separation [5]. Uranium is also a starting material for the fabrication of several alloys, which are employed as fuels in different reactors.

The uranium metal rods/ingots fabricated will be left with a few non metallic impurities like hydrogen, nitrogen, oxygen and carbon [6], in either free or combined form. The free gaseous impurities will be present as occluded gases trapped in the interstitial spaces of the metal matrix. During heating of the metal, the occluded gases will be released. At higher temperatures, UH and UN will decompose to give H_2 and N_2, and $[UO]_U$ reacts with $[UC]_U$ to form CO_2 and/or CO depending on the temperature [7]. All these gaseous products will cause pressure build-up in the hermetically sealed fuel pin. In the AVLIS technique of enrichment, adequate uranium vapour pressure ($\sim$10 Pa) is to be maintained. In the actual practice, large quantities of uranium metal are heated to $\sim$2500 K, under vacuum to achieve the required vapour pressure of uranium. The gases released from uranium metal deteriorate the efficiency of furnace and the pumping system wherein the evaporation of uranium is taking place.

In the nuclear reactors, the temperature to which the fuel reaches, is dictated by the operating conditions of the reactor, the clad, the coolant and the thermal conductivity of the fuel, while in AVLIS it is heated to $\sim$2500 K. Thus it is seen that, uranium gets heated to different temperatures, depending on the application.

It is, therefore, essential to have a knowledge of the total amount and the composition of gases released from uranium, at different temperatures. With this in view, exhaustive studies have been carried out, over a temperature range 873–1500 K, employing hot vacuum extraction followed by quadrupole mass spectrometry. The upper limit of temperature is chosen so as to carry out the experiments up to near melting temperature of uranium metal. The present paper deals in detail about the temperature calibration of the system and computation of the composition and the concentration of released gases, from the mass spectral data, the fragmentation coefficients and the respective relative sensitivity factors.

2. Experimental

2.1. Equipment

Leybold Heraeus, total gas analyser Model VH-9S has been employed in all the experiments. Schematic diagram of the system is shown in Fig. 1. Total gas analyser is essentially a static ultra high vacuum system. Since the amount of total gas content is very small, the equipment should hold the vacuum under static conditions for several hours. Detailed description of the equipment is given elsewhere [7].

Optical pyrometer (PYRO micro optical pyrometer, USA) and Dataquad DXM quadrupole mass spectrometer, UK were employed for measuring the temperature and composition, respectively.

2.2. Procedure

2.2.1. Sample preparation

Two batches of uranium samples (a) 10 mm long, 3 mm dia and weighing about 3.0 g each and (b) 5 mm long, 3 mm dia and weighing about 1.5 g were taken from same lot of uranium rod. To minimize the contamination of the system and the tungsten crucible with uranium vapour and with molten uranium, uranium metal aliquot is taken in double containment. The sample is taken in tantalum cup and is closed with a lid having 1 mm circular hole. This is enclosed in another tantalum crucible. The above setup is loaded in the tungsten crucible and covered with tungsten lid having three 1 mm dia circular holes. The crucible arrangement is shown in Fig. 2. The vapour pressure of uranium is low (3.95×10^{-7} Pa at 1500 K). Since the holes in the lids (tantalum lid and tungsten lid) are not in same line, most of the uranium vapour will hit the container or the lid and the possibility of the vapour coming out, is reduced. In the experiments carried out above the melting temperature of uranium, liquid uranium metal will be contained in the tantalum crucible and will not come in direct contact with the tungsten crucible.

2.2.2. Sample loading

The sample taken in the tantalum crucible assembly, is loaded in a tungsten crucible by opening the sample port in a flow of inert gas. The tungsten crucible is closed with a tungsten lid having three 1 mm dia holes. The complete crucible assembly is transported to the heating zone employing vertical, horizontal and angular vacuum manipulators. The system is evacuated and degassed at room temperature for 2–3 h at 10^{-3} Pa.

2.2.3. Gas extraction

The sample is heated to the required temperature and time by induction heating. The temperature is measured by optical pyrometer. The gases released are extracted employing mercury ejector pump, into a pre-calibrated volume through a refrigerated cold trap (to remove condensable gases). For the absolute and accurate measurement of the pressure exerted, a McLeod gauge is used. Small amount of this gas is then fed into the electron impact ion source of on-line quadrupole mass spectrometer, through a micro leak valve and several spectra are scanned.

2.2.4. Temperature calibration

Heating of the sample (contained in tungsten crucible) is carried out by water cooled induction heating of 330 kHz frequency. The temperature is varied by suitably selecting the anode current and anode voltages of the induction coil, using power regulation potentiometer. A disappearing filament type optical pyrometer is employed to measure the temperature. To achieve the black body conditions, to the maximum possible extent, the tungsten crucible is covered with a tungsten lid having three 1 mm dia holes, and the optical pyrometer is focused through one of the