Spatial profile studies of nuclear material burn-up by Laser Ablation-Ionization

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1. Abstract

Measurement of ^{10}B consumption in FBTR control rod samples using TOF Mass spectrometer as well as a method to measure the burn up using Pulsed Laser Deposition (PLD) of thin films, followed by TIMS is described in this work. Unlike the traditional PLD techniques, we used high laser power density and deposited films with more particulates such that the elemental fractionation is greatly minimized in the subsequent mass spectrometer analysis. An added advantage of sampling using focused laser is the possibility of surface profiling of elements for post-irradiation examination of chemical and isotope mapping of surfaces at a typical "pixel" resolution of the laser spot size. The nano-gram quantities of such sampling contain very low activity, resulting less tedious radioactivity handling.

Conventional chemical dissolution method for nuclear fuel burn-up involves many steps such as separation of U, Pu and burn-up monitor fractions, followed by isotope dilution mass spectrometry (IDMS)[1,2], which is more laborious and carries risk of radiation exposure to workers. Sampling of solids by Laser ablation (LA) is a convenient method for direct burn-up measurement of irradiated fuel as well as control rod pellets [3, 4, 5]. Using suitable optics, laser beam can be conveniently taken inside hot cells for sampling the surface of highly radioactive materials [4, 6]. Added advantage of LA technique is the laser spot profiling and hence the post-irradiation examination of chemical and isotope mapping of surfaces at a typical "pixel" resolution of 50-100 sq micron size. The nano-gram quantities of such sampling contains very little activity and hence can be conveniently handled in a glove box and adds very less load to the radioactive laboratory exhaust processing systems.

The present work describes burn-up characterization of simulated spent fuel at different irradiation level of uranium oxide containing rare earth fission products and actual irradiated B4C control rod pellets discharged from Fast Breeder Test Reactor, Kalpakkam. Simulated spent fuels were prepared in pellet form and pulsed laser deposition (PLD) of thin films were carried out using laser pulses at different laser fluence (power density is most appropriate term to compare lasers of different pulse width) and wavelengths. The thin films were then dissolved in nitric acid and isotope ratios of different elements with respect to uranium (uranium to Nd-143 & La-139) were analyzed using Thermal Ionization Mass Spectrometer (TIMS) and Inductively Coupled Plasma Mass Spectrometer (ICPMS). Similar isotope ratios were also measured by loading the simulated solid pellets directly in an in-house developed Laser ionization-Reflectron Time of Flight Mass Spectrometer (L-RTOFMS).

Two different analytical approaches; the first directly employs the home built Reflectron Time of Flight Mass Spectrometer with Laser as the ion source (L-RTOFMS), whereas the second approach uses laser ablation as a sample collection technique for further analysis using a multi-collector TIMS and Inductively Coupled Plasma as ion sources. The lasers used were (i) a commercial flash lamp pumped Q-switched Nd-YAG laser with a pulse width of 8ns, (ii) a custom made laser having pulse width of about 100ps and (iii) KrF Excimer Laser 248 nm, 30 nanosec FWHM [7].

Schematic of the L-RTOFMS used for studying the spatial profile of the elemental isotopes is shown in Fig.1. This facility is built in-house with the sample chamber and sample loading and manipulator parts inside a Shielded Glove box in order to study the consumption of ^{10}B in the B4C control rod pellet used in the Fast Breeder Test Reactor (FBTR). The line sketch in the right side of Fig 1 is the ion trajectory curve obtained using SIMION program to design the L-RTOFMS [8]. The control rod stack containing the B_4C pellets has served an effective full power operation of 653 days and was discharged from the core after a peak fuel burn-up of 102 GWd/t [3]. Though Boron and Carbon do not become active in view of the (n,α) reactions, the presence of trace impurities makes the B_4C pellets active and hence need to be handled inside a Glove box.

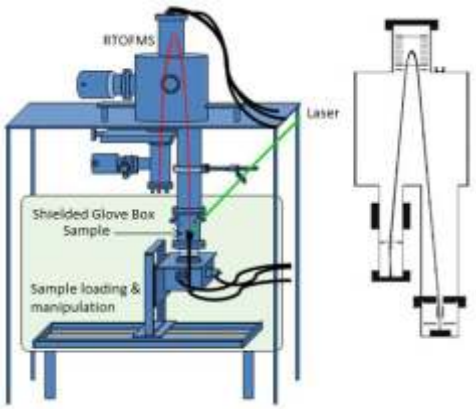

Fig.1 Schematic setup used to measure boron isotope ratios in the irradiated control rod pellets.

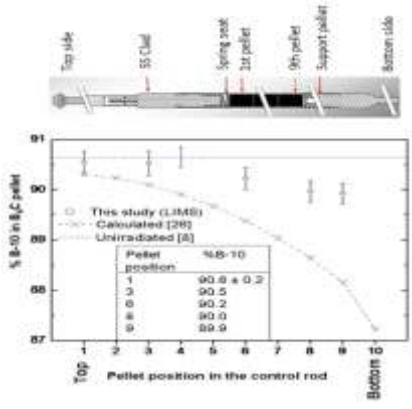

Fig.2 (Right) Schematic of B4C pellets in the FBTR control rod and the consumption pattern of ^{10}B

Each control rod has a stack of 9 pellets, out of which the bottom most pellets are exposed to higher neutron flux hence 10B is consumed more. Since B_4C enriched with 90% ^{10}B, each pellet is precious and the present experiment is aimed to identify the pellets for re-use. Top portion in Fig.2 displays the schematic of B_4C pellets in the FBTR control rod and the bottom graph shows the consumption pattern of ^{10}B. The dotted curve is the theoretical modelling of the consumption pattern at the fuel burn-up level at which this rod was discharged. Our experiment revealed that the maximum consumption occurred for the bottom most pellet is within 1% and even the bottom most pellet can be reused.

Laser vapourization-ionization studies [9, 10, 11] showed that the elemental species composition in the laser plume is governed by the laser ablation process, which greatly vary on the laser conditions. Even the isotope composition is found influenced by laser fluence [11, 12], especially under tight laser focusing conditions. A laser power density > 10^8 W/cm^2 on the target surface results in the enrichment of lower mass species towards the axial direction of the laser plume and hence a typical power density about 10^7 W/cm^2 was recommended for isotope ratio analysis in L-RTOFMS.

However, the laser ablation process under this power density makes thermal vapourization to dominate the ablation process [9] and results in elemental fractionation in the laser plume. Hence laser ablation under a non-thermal process (or forced congruent evaporation) is preferred over thermal ablation for analytical studies in order to minimize elemental fractionation. Such non-thermal laser ablation also causes ejection of micron sized particulates, often a large quantity of materials is removed from target surface through particulate ejection process [13]. Hence, PLD is an ideal analytical technique which exploits the collection of total material removed including particulates for elemental composition analysis.

Thin films were deposited by PLD technique using (i) Q-switched Nd-YAG laser of wave length 1064nm and 532nm with a pulse width of 8 ns, (ii) Picosecond Nd-YAG laser with 1064nm, 532nm and 266nm with a pulse width of 100 ps and (iii) Excimer laser at 248nm with a pulse width of 30 ns. A quartz lens with a focal length of 50 cm was used for focusing the laser beam and the target was positioned after the focus. The substrate-target distance was maintained 2.5cm. The focal area was kept such that power density is $1x10^8$ W/cm^2. The depositions were carried out at rough vacuum, as the ultimate application is for analyzing radioactive sample – i.e. handing under rough vacuum is easier than high vacuum condition. The plume produced was deposited on a glass plate and the deposit was dissolved in minimum quantity of QD nitric acid and was evaporated to dryness. The residue was dissolved in minimum volume of dil. nitric acid (strictly to the volume essentially required for isotopic dilution) for TIMS analysis. For ICPMS analysis, the deposited material was dissolved in minimum quantity of QD nitric acid and the dissolved solution was dried and the residue was re-dissolved in dilute nitric acid(1%) and was subjected to analysis by ICP-MS for isotopic ratio measurement. Fig. 3 shows the least elemental fractionations are observed for samples deposited using lasers at UV wavelengths.

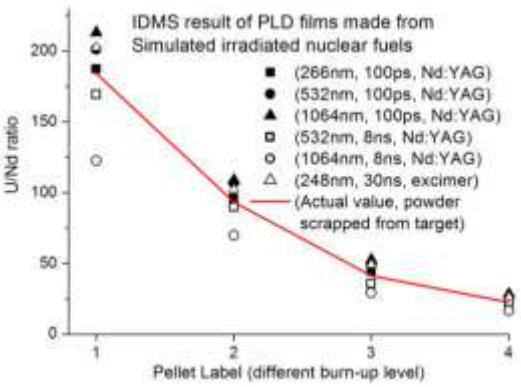

Fig.3 Isotope Dilution Mass Spectrometry studies by TIMS on dissolved the PLD films of simulated irradiated fuel.

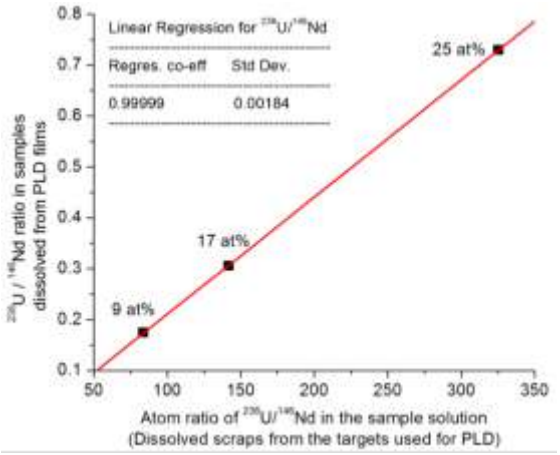

Fig.4 Burn-up measurements on dissolved PLD films of simulated irradiated fuel at different burn-up conditions.

In the case of UO_2 based fuel samples we tried to exploit the forced congruency and particulate ejection behavior towards quantitative analysis. Since Nd is used as burn up monitor in nuclear fuel burn up studies, simulated fuel pellets of UO_2 with different concentrations of natural Nd is prepared for use as laser targets to make thin films by PLD process.

Since ICPMS is a more versatile technique in view of its ability to produce ionization close to unity, the PLD films in dissolved nitric acid prepared as above is analyzed using ICPMS. Fig. 4 shows the results obtained for the burn up measurement standards covering a wide range of burn up levels of interest after the standardized data processing [14]. The linear fit of the normalized counts against the actual samples taken in the solution shows an regression co-efficient close to unity. The regression co-efficient in this case is unity, indicating that the PLD films represents the elemental composition same as that of the target pellet. In other words, the experiments shows that the elemental fractionation problem, considered to be a deterent getting stoichiometric elemental composition in laser ablation, can be solved.

The present work shows the measurement of 10^B consumption in FBTR control rod samples as well as describe the method to measure the burn up using laser ablation. Unlike the traditional PLD techniques, we used high laser power density and deposited films with more particulates such that the elemental fractionation is greatly minimized in the mass spectrometer analysis. Moreover the present work does not use complex laser beam shaping optics and laser beam engineering arrangements and hence taking the laser beam inside very thick radiation shielding is relatively easy, hence most convenient for quick burn up analysis of irradiated nuclear fuels.

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