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X-ray fluorescence and absorption analysis of krypton in irradiated nuclear fuel

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ABSTRACT

The analysis of krypton in irradiated uranium dioxide fuel has been successfully achieved by X-ray fluorescence and X-ray absorption. The present study focuses on the analytical challenge of sample and sub-sample production to perform the analysis with the restricted conditions dictated by the radioprotection regulations. It deals also with all potential interferences that could affect the quality of the measurement in fluorescence as well as in absorption mode. The impacts of all dissolved gases in the fuel matrix are accounted for the analytical result quantification. The krypton atomic environment is ruled by the presence of xenon. Other gases such as residual argon and traces of helium or hydrogen are negligible. The results are given in term of density for krypton ($\sim$3 nm^{-3}) and xenon ($\sim$20 nm^{-3}). The presence of dissolved, interstitial and nano-phases are discussed together with other analytical techniques that could be applied to gain information on fission gas behaviour in nuclear fuels.

1. Introduction

The most widely used nuclear fuel material, uranium dioxide, undergoes production of a wide variety of elements during irradiation in nuclear reactors. Among the elements produced by binary fission are rare gases such as Xe and in a lower fraction Kr. Part of these fission gases are weakly soluble and are potentially diffusing, part segregates as nanometre sized phases called bubbles. Their occurrence is well known and their release properties have been reported [1–3].

The behaviour of fission gas in high burn-up fuel during steady-state and transient conditions is of special interest for safety reasons. According to the defect-trap theory for fission-gas release the escape rate of gas atoms from UO_2 is controlled by the number of defects in the UO_2 structure. To test this theory the release rate of fission gas from single crystal UO_2 was compared to that from fine-grain UO_2. Considering the specific conditions it could be shown that fine grained UO_2, representing a higher trap density, better retain fission gas [4]. However, transients were not applied.

A dynamic method to study the release of fission gases from UO_2 fuel during low temperature irradiation was presented [5] confirming the theory based on a defect-trap model and the knock-out process. It supports also the assumptions that gas in an intermediate state exists as dissolved fission gas and as trapped in 'bubbles'. The dynamic method gives a satisfactory qualitative and quantitative interpretation of the transient fission gas release for a step function of fission rate. The predominant mode of release is single gas atom diffusion to free surfaces with a small, but burn-up-dependent contribution from direct recoil. This is confirmed in another publication [6] where the measurements of longer-lived fission products (Fp) indicated that their release appeared to be controlled by diffusion.

An accurate mechanistic model that reflects the fission gas transport process and reliably predicts the evolution of the remaining fission gas in the high burn-up structure (HBS) was missing. This problem was approached by developing a one-dimensional, mass balance model. It was applied to light water reactor (LWR) UO_2 fuel at the moderate temperatures found in the periphery (rim) region [7]. The model that incorporates a two-step burn-up factor in the two-stage diffusion processes in the grain lattice and at the grain boundary during the fission gas release was proposed. Results showed that the predictions were in better agreement with the experimental measurements than those of any other models built in the code over the entire burn-up range up to 75 MW d kg^{-1} [8]. More recently, a comprehensive model (GRSW-A) was

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developed to analyse the processes of fission gas release, gaseous swelling and microstructural evolutions in the uranium dioxide fuel during base irradiation and under transient conditions [9]. The GRSW-A analysis incorporates a number of models published in open literature. The most prominent aspects of GRSW-A and its coupling with the FALCON fuel behaviour code allows the analysis of fuel such a fuel segment irradiated in pressurized water reactor (PWR) to a burn-up of about 50 MW d kg^{-1}. Besides, the generalised data on fission gas release in PWR fuel during the base irradiation up to a burn-up of ~70 MW d kg^{-1} was interpreted.

The development of these models require, however, experimental evidences that are closely linked to the analytical tools provided today. The fission gas analyses are mostly carried by post irradiation examination (PIE) techniques such as gamma scanning, mass spectroscopic analysis and/or micro-structural analyses. Gamma scanning is currently performed in the reactor pool and on-site γ-ray spectroscopic measurements of fission gas release in irradiated nuclear fuel has been reported [10].

PIE off-line is carried out on selected fuel material samples. Fuel rod puncturing and subsequent mass spectroscopic investigation of the released gas deliver integral information about the gaseous fission products yield in the rod. Secondary ion mass spectrometry was used for measurement of fission gas radial distribution in UO_2 nuclear fuel [11]. Mass and gamma spectrometry were combined for the measurement of fission products released from overheated, freshly irradiated, uranium dioxide [12]. Small UO_2 spheres were completely evaporated in a tungsten crucible shortly after irradiation, followed by monitoring with a germanium gamma spectrometer and with a quadrupole mass spectrometer. In addition, fission gases released from irradiated nuclear fuel were analysed for Kr and Xe by gas chromatography [13].

Micro-structural analyses have been carried out by electron probe microanalysis (EPMA) and transmission electron microscopy (TEM). The accurate analysis of locally retained fission gas in nuclear fuel is inherently difficult since the physical form under which it is stored varies from an atomic dispersion to 'bubbles' with a diameter of several hundreds of nanometres. EPMA is difficult to apply in a quantitative manner if the studied materials are inhomogeneous at the scale of the electron–solid interaction volume. A method was developed to analyse a system of gas 'bubbles' distributed in irradiated nuclear fuel [14]. The microstructural changes in commercial light-water reactor (LWR) fuels irradiated to average burn-ups near 50 MW d kg^{-1} were also studied by TEM and Auger electron spectrometry. Several poorly understood aspects of the fuel behaviour were examined, including precipitation of the fission gases in dense, highly pressurised inclusions, in the UO_2 matrix, and the "rim effect" involving restructuring of the enhanced burn-up region at the fuel outer edges [15].

A TEM and thermal desorption spectroscopy (TDS) study of gas release from 'bubbles' in krypton-implanted uranium dioxide was also carried out. The release of gas atoms from 'bubbles' at high temperatures challenges the older assumption that the solubility of xenon and krypton in UO_2 is effectively zero. The results and conclusions of experimental work designed primarily to resolve the competition between two mechanisms [16]. To avoid the difficulties inherent in experiments with nuclear fuel, the experimental approach used ion implantation techniques to form 'bubbles' in UO_2 samples which were then examined with TEM and TDS during annealing to high temperatures. This combination of techniques allowed 'bubble' substructure changes to be correlated with gas release. In spite of conditions chosen to optimise the detection of thermal resolution, no positive indications of this mechanism were observed at that time and for the studied system. More recently, the analysis of xenon gas inclusion in irradiated nuclear fuel by laser ablation ICP-MS revealed its isotopic composition and subsequently allowed estimation of the pressure in microscopic 'bubbles' [17].

However, in-pile diffusion of fission gas is generally modelled through an effective diffusion coefficient that must take into account various phenomena occurring at the grain scale. One of these relates to the trapping of gas by intragranular bubbles. This trapping is only temporary, because the gas is brought back into atomic solution through interactions with fission fragments or fast neutrons, the so-called resolution process [18]. This resolution process was investigated with molecular dynamics techniques. For low-energy interactions (<50 keV), the collision cascades caused by a single fast moving primary knock-on atom (PKA) were studied. The higher energy range was studied by the thermal spike method. The studies shed light on the atomic scale processes at play for fission gas resolution in nuclear fuel. The high energy interactions destroy smaller 'bubbles' completely and bring a quasi-constant number of gas atoms in resolution when they interact with larger bubbles.

None of the above mentioned techniques allows the characterisation of the krypton atomic environment in the uranium dioxide material. The purpose of this study is to investigate by X-ray absorption fine structure (XAFS) spectroscopy the atomic environment of krypton as fission gas from binary fission in the uranium dioxide fuel pellet irradiated at a standard burn-up of around 40 MW d kg^{-1}.

2. Experimental

2.1. Sample

For the present investigations the specimen was a standard uranium dioxide fuel. The fuel material was irradiated for 3 cycles in a commercial pressurized water reactor (PWR) up to an average burn-up of ~39.5 MW d kg^{-1}. After a certain time in the spent fuel pool, it was transported to the PSI Hot Laboratory. The sample preparation was carried out in a hot cell. As a first step of investigation scanning electron microscopy (SEM) and electron microprobe analysis (EPMA) images of the grain structures and composition of fuel pellets were taken. A preparation of subsample (fuel particles on Kapton) was needed, due to the fact that at the used synchrotron source (Swiss Light Source: SLS) beam line (microXAS beam line) an activity below 100 LA (limite d'authorisation) is permitted. Detailed information of the analysed fuel pellet and the subsample is provided in Table 1.

Because of the limited activity for specimens allowed in the microXAS hutch at the synchrotron facility, small particle samples are necessary for the investigation. A specific preparation of the subsample of fuel is required. Fig. 1 depicts the replicate technique used for the preparation of a subsample.

The azimuthal resolution of grinding is about 30°, with a radial resolution estimated to be better than 1 mm. The area size of origin uncertainty on the prepared sample is then of the order of 1 mm^2. Since the activity on the replicate of the fuel cross section is generally too large cutting of a stripe (subsample) is required. The stripe selected for the analysis was 2.4 mm × 2.2 mm in size, corresponding to the periphery of the fuel. The particle analysed is located at about 1 mm from the rim in a position corresponding to a local burnup of 44.0 MW d kg^{-1} and a plateau in the fission product concentration (see Table 1). This plateau is to be found from the rim to about 2.2 mm in pellet radial distance prior to the thermal depleted part in the pellet centre.

Some aspects of the sample preparation and analysis were reported previously [19,20]. The stripe mounted in the analytical cell and set in the sample holder (see Fig. 2) was transferred to the synchrotron light source for analysis. The dose rate at 1 cm was 60 μSv h^{-1}.