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Characterization of un-irradiated MIMAS MOX fuel by Raman spectroscopy and EPMA

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ABSTRACT

In this study, Raman spectroscopy technique was implemented to characterize un-irradiated MIMAS (MIcronized - MASter blend) MOX fuel samples with average 7 wt.% Pu content and different damage levels, 13 years after fabrication, one year after thermal recovery and soon after annealing, respectively. The impacts of local Pu content, deviation from stoichiometry and self-radiation damage on Raman spectrum of the studied MIMAS MOX samples were assessed. MIMAS MOX fuel has three different phases Pu-rich agglomerate, coating phase and uranium matrix. In order to distinguish these phases, Raman results were associated with Pu content measurements performed by Electron Microprobe Analysis. Raman results show that T_{2g} frequency significantly shifts from 445 to 453 cm^{-1} for Pu contents increasing from 0.2 to 25 wt.%. These data are satisfactorily consistent with the calculations obtained with Gruneisen parameters. It was concluded that the position of the T_{2g} band is mainly controlled by Pu content and self-radiation damage. Deviation from stoichiometry does not have a significant influence on T_{2g} band position. Self-radiation damage leads to a shift of T_{2g} band towards lower frequency (~1–2 cm^{-1} for the UO_2 matrix of damaged sample). However, this shift is difficult to quantify for the coating phase and Pu agglomerates given the dispersion of high Pu concentrations. In addition, 525 cm^{-1} band, which was attributed to sub-stoichiometric structural defects, is presented for the first time for the self-radiation damaged MOX sample. Thanks to the different oxidation resistance of each phase, it was shown that laser induced oxidation could be alternatively used to identify the phases. It is demonstrated that micro-Raman spectroscopy is an efficient technique for the characterization of heterogeneous MOX samples, due to its low spatial resolution.

1. Introduction

Mixed (U, Pu)O_2 oxides are widely used in the nuclear industry, and therefore, it is essential to understand their ageing processes. These mixed oxides can be subjected to various media (air, water, steam, etc.) and stresses (irradiation, oxidation, etc.), which can affect their reactivity and/or accelerate their corrosion. One of the most interesting mixed oxide material to investigate is the commercial MIMAS MOX fuel produced in France [1]. This fuel is produced by a two-step process consisting of blending and milling of UO_2 and PuO_2 powders (master mix), followed by dilution with UO_2 until the desired U/Pu ratio is achieved. The close contact between the micronized UO_2 and PuO_2 particles provides adequate interdiffusion during the sintering and therefore, the required solubility of Pu into the UO_2 matrix [2]. The fabrication process has a strong impact on the microstructure of MIMAS MOX pellets. In particular, the microstructure of MOX pellets prepared with UO_2 powder from the ammonium diuranate (ADU) process have three different phases; a plutonium rich phase named “agglomerate”, a uranium rich one named “UO_2 matrix” and a “coating phase” with intermediate Pu content. In a different manner MOX pellets prepared with the ammonium uranyl carbonate (AUC) process show only two phases; “plutonium agglomerate” and a “UO_2 matrix” [3]. This heterogeneous microstructure represents the major difficulty for the characterization of MOX fuels.

Experimental techniques have been developed in recent years to provide structural data on such radioactive materials. One of these

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techniques is Raman spectroscopy, which provides relevant data on the structural changes occurring on the surface of polycrystalline materials at micrometer scale. Raman spectroscopy is particularly attractive technique compare to the others (such as X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS), X-ray photoelectron spectroscopy (XPS), electron probe microanalyzer (EPMA), transmission electron microscopy (TEM)), due to the its ability to perform in-situ and ex-situ investigation of highly radioactive samples. In addition, it does not require any sample preparation step. Several studies have been published so far related to the Raman spectrum of UO_2 [4–14] but only a few studies have been published related to the characterization of mixed actinide oxides such as $(U_{1-y}, Pu_y)O_2$, $U_{1-x}Th_xO_2$ and $U_{1-x}Am_xO_2$ by Raman spectroscopy [15–20]. In our previous study, it was illustrated the efficiency of Raman spectroscopy technique for the characterization of an un-irradiated homogeneous $U_{0.76}Pu_{0.24}O_{2+x}$ sample, which had been stored for 30 years under air [21]. In this work the un-irradiated heterogeneous MIMAS MOX samples was investigated with EPMA, XRD and Raman Spectroscopy. In particular, it was aimed to characterize its three different phases (UO_2 matrix, coating phase and Pu agglomerate) and to study the effects of Pu content, self-radiation damage and non-stoichiometry on the Raman spectra of each phase.

2. Experimental

2.1. Material

MIMAS MOX fuels, containing an average of ~7 wt.% of Pu were fabricated with ADU process in June 2000 at Marcoule Melox plant. The initial isotopic composition of the MIMAS MOX fuel (in June 2000) is given in Table 1. The fuel was stored over 13 years at room temperature under air and then was cut into 8 mm diameter and 2 mm thickness disks. All the disks were optically polished on one side and three of them were used in this study.

Damaged MIMAS-MOX: the first disk was analysed 13 years after fabrication by EPMA. Raman spectroscopy characterization was performed 1 year after EPMA measurement.

Annealed MIMAS-MOX 1: the second and third disks were annealed at 1273 K for 16 h under Ar/H_2 (5%) atmosphere, with an O_2 potential of −375 kJ/mol, imposed by H_2/H_2O equilibrium (humidity: 20000 ppm H_2O). The aim of this annealing was to restore the stoichiometry and to recover the radiation damage formed during the 13 years of storage [22,23]. However, the annealed disk could only be characterized by Raman spectroscopy one year after annealing. Therefore, these characterizations correspond to a partially aged sample with possible effects of radiation damage and surface oxidation.

Annealed MIMAS-MOX 2: To fully recover the material and avoid any effects of surface oxidation and radiation damage, the third disk was annealed a second time. XRD and Raman characterizations were performed soon after annealing.

2.2. Characterization techniques

2.2.1. Electron probe micro-analyzer

Electron probe micro-analyzer (EPMA, CAMECA SX 50, Cameca, France) was used to determine the distributions of Pu in the damaged MIMAS MOX sample with a spatial resolution of 1 μm. The EPMA was equipped with four X-ray spectrometers and TAP/PET crystals and operated under an acceleration voltage of 20 kV and 20 nA stabilized beam. To quantify the Pu content, the instrument was calibrated with plutonium-bearing glasses material (1.74 wt.% Pu) [24]. Pu content of the reference material was determined by calorimetry. Instrumental uncertainty on concentration measurements is equal to ± 5%. Sample used to the EPMA investigation was embedded with epoxy resin in a sample holder and its surface was polished using a diamond paste of 1 μm grain size.

2.2.2. X-ray diffraction

Powder X-ray diffraction was used to analyse the lattice parameters of the annealed MIMAS MOX 2 sample. The sample was placed in a stainless steel container with a beryllium window transparent to X-rays, and the container was then attached to the diffractometer D8 Advance (Bruker) by using a copper radiation tube source ($K_{\alpha1}$ and $K_{\alpha2}$: 1.5406 and 1.5444 Å, respectively). Rietveld refinements of the compounds were performed with the Fullprof program [25,26] included in the WINPLOTR software [27]. The line profile shapes are described by a modified Thompson–Cox–Hastings pseudo-Voigt function. The background was approximated by a Chebyshev polynomial function with three terms. The refinement procedure first considers the zero detector and background parameters, then lattice parameter and crystallite size. The uncertainty on the lattice parameter was estimated to be less than 0.001 Å.

2.2.3. Raman spectroscopy

A Horiba LabRam-HR800 Raman spectrometer coupled to a nuclearized optical microscope (Optique Peter, Lyon, France) was used. The instrument has been adapted for the examination of radioactive materials in Atalante hotcell facility [15]. A YAG laser (532 nm), which powers output could be adjusted using different filters, was used as an excitation source. The laser was focused to a spot size of around 1 μm with a 100x objective; the incident laser power was about 2.8 mW. The spectrograph angle was calibrated with the T_{2g} mode of a silicon single crystal, set at 520.5 cm^{-1} [28]. The spectral data were acquired with an exposure time of 300–600 s over the wavenumber range from 100 to 1800 cm^{-1}. It was experimentally found by changing laser power and acquisition time that 2.8 mW laser power for 600 s acquisition time has no detectable oxidation effects on the material surface. Laser-induced oxidation tests were also performed by adjusting the laser power at about 19 mW and with 60 s of exposure time. Raman spectra were recorded before and after oxidation with 2.8 mW laser power for 600 s. The Lorentzian peak model and spline baseline correction were used to deconvolute the Raman peaks. Based on the position of the silicon band and the calibration, the instrumental resolution is about 0.7 cm^{-1}.

Table 1
Initial isotopic composition of MIMAS MOX fuel with average 7 wt.% Pu.

Isotopic Pu composition (%)						Isotopic U composition (%)
$^{238}Pu/Pu$	$^{239}Pu/Pu$	$^{240}Pu/Pu$	$^{241}Pu/Pu$	$^{242}Pu/Pu$	$^{241}Am/Pu$	$^{235}U/U$
1.72	58.06	25.51	6.8	6.2	1.65	0.25