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Thermal effects on mass and spatial resolution during laser pulse atom probe tomography of cerium oxide

Rita Kirchhofer [a,*], Melissa C. Teague [b], Brian P. Gorman [a]

[a] Colorado Center for Advanced Ceramics, Metallurgical and Materials Engineering, Colorado School of Mines, Golden, CO, USA
[b] Fuel Performance and Design, Idaho National Laboratory, Idaho Falls, ID, USA

HIGHLIGHTS

- Cerium oxide, a surrogate for nuclear fuels, was used for atom probe tomography.
- Stoichiometric field evaporation of CeO_2 was produced using laser pulsed APT.
- The effect of laser energy and specimen base temperature was studied.
- Mass resolving power was optimized for the run conditions with high specimen yield.
- Spatial resolution in the nm-scale was maximized by reducing laser energy.

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ABSTRACT

Cerium oxide (CeO_2) is an ideal surrogate material for trans-uranic elements and fission products found in nuclear fuels due to similarities in their thermal properties; therefore, cerium oxide was used to determine the best run condition for atom probe tomography (APT) of nuclear fuels. Laser-assisted APT is a technique that allows for spatial resolution in the nm scale and isotopic/elemental chemical identification. A systematic study of the impact of laser pulse energy and specimen base temperature on the mass resolution, measurement of stoichiometry, multiple detector hits, and evaporation mechanisms are reported in this paper. It was demonstrated that using laser-assisted APT stoichiometric field evaporation of cerium oxide was achieved at 1 pJ laser pulse energy and 20 K specimen base temperature.

1. Introduction

The increasing demand for cost effective green energy has led to a renewed interest in nuclear energy, including the commercialization of fast breeder reactors (FBRs) [1,2]. In order for FBRs to become economically competitive with current light water reactors (LWRs) the average burn-up of fuel assemblies in an FBR will need to exceed ~150 GWd/tHM (~15% FIMA) [3]. A secondary reason for interest in FBRs is in their potential to "burn" or transmute long-lived transuranic isotopes contained in spent nuclear fuel produced by the current fleet of LWRs [2,4]. Mixed oxide (MOX) fuel consisting of $(U, Pu)O_2$ is a promising fuel for use in FBRs but its performance at high burn-up is not well understood. The distribution of fission products within the fuel element is necessary to understand the performance at higher burn-ups. Atom probe tomography can provide spatial resolution in the nm-range and isotopic/elemental data of the distribution of fission products within irradiated fuel that cannot be obtained from any other current analytical technique [5]. Due to the difficulty in handling and making irradiated MOX fuel samples a graded approach to developing appropriate atom probe techniques was selected. Cerium oxide (CeO_2) can be used as a surrogate material for trans-uranic elements found in nuclear fuels and the fission products present post-irradiation due to similarities in their thermal properties; therefore, it was selected for initial parameter studies on the atom probe [6].

Only a limited amount of experience running insulating ceramic materials in the atom probe exists [7–11,14]. It is generally accepted that a thermal event from the laser pulse causes localized heating of the tip due to the absorption of the laser and assists in field evaporation by reducing the field needed for field emission of ions [5,11–13]. Laser-assisted APT is strongly influenced by the absorption characteristics of the material (e.g. band gap); the physical mechanisms of field emission in wide band gap materials are not fully understood but the interaction of the laser with the nm-sized specimen results in field emission [7,12,13]. Previous work on ceramics has resulted in time-of-flight (TOF) mass spectrum data with poor mass resolving power at different laser energies and wavelengths [7,8,14]. The reported mass resolving power ($m/\Delta m$) in Ref. [9] was between 450 and 490. It was also demonstrated that correct stoichiometry for the specimen could be ob-

* Corresponding author. Tel.: +1 530 219 9831.
E-mail address: rkirchho@mines.edu (R. Kirchhofer).

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tained but that that the laser pulse energy had a great effect, while the specimen base temperature affected the signal-to-noise ratio. Correct stoichiometry was obtained for the specimens reported in Ref. [9] however, the mass spectrum ranging protocol was not explained and atom probe tomography data is highly sensitive to assigned ranges [7]; furthermore, the treatment of the 16 Da peak, which can be assigned as the O^+ ion and/or the O_2^{++} cluster, was not detailed in the referenced work. Good mass resolving power is critical to perform quantitative analysis of complex systems such as irradiated fuel that have overlapping peaks in the mass spectra. In order to accurately determine the chemical composition and internal structure of a sample in the atom probe, it is necessary to find run conditions that yield even evaporation of ionic species and minimize surface diffusion, which increases spatial resolution.

An investigation of optimal running condition was required to understand the field evaporation behavior of cerium oxide as a surrogate for MOX fuel. A systematic study of the impact of laser pulse energy and specimen base temperature on the mass resolution, measurement of stoichiometry, multiple detector hits during a single evaporation pulse, and evaporation mechanisms are reported in this paper.

2. Experimental set up

Atom probe specimens were prepared from a bulk sample of cerium oxide with a dual-beam FEI Quanta 3D FEG using a standard wedge lift-out technique and annular milling patterns to create the specimens [15]. The cerium oxide specimens were mounted onto a copper mesh grid that had been sectioned and each post pre-thinned in the dual-beam [16]. The specimens were placed on a TEM/APT compatible holder that allows for cross-correlative analysis between the TEM for imaging, and the atom probe for elemental characterization [15–18]. The atom probe specimens were prepared in such way that the tip radius was between 48 nm and 68 nm and shank angle of ~25° was obtained for more efficient heat transfer from the tip to the bulk of the specimen. TEM images were acquired in an FEI Tecnai F30 or a Phillips CM200 transmission electron microscope. TEM micrographs of a representative atom probe specimen before and after analysis are shown in Fig. 1. The tip radius and shank angle measurements were performed from the TEM micrographs of the specimens.

Laser-assisted APT was performed in a Cameca LEAP 4000X HR or LEAP 4000X Si system equipped with a UV laser (wavelength 355 nm) and spot size less than 1 μm. The HR system used for these experiments has a detection efficiency of approximately 37%, while the Si system has a straight flight path and higher detector efficiency at 57%. The mass resolving power of the HR set up is greater than for the Si system. The laser energy was adjusted between 1 pJ and 1000 pJ per pulse at 100 kHz laser pulse rate for a specimen base temperature of 20 K; the laser energy was set at 1 pJ, 10 pJ, and 100 pJ per pulse for specimen base temperatures of 70 K using 100 kHz laser pulse rate as well.

Data analysis was performed using Cameca IVAS™ v.3.6.2 software. For the composition analysis all the runs were manually ranged at full-width tenth maximum (FWTM) of the peak (the intensity of each peak was determined and the upper and lower bounds for the ranges were set at 10% of the maximum counts) for the decomposition analysis of the mass spectrum. Peaks with intensity less than 1% of the full intensity of the highest peak (usually O_2^+) were not manually ranged but the software automatically assigned ranges to the identified ions or ionic clusters. Isotopic peak overlap was minimum due to the simple mass spectrum of the binary oxide. However, the oxygen peak at 16 Da was ranged as both the O^+ ion and the O_2^{++} cluster for the decomposition analysis presented in this work in order to obtain the correct stoichiometry for the oxide. The ionic fraction of O^+ and O_2^{++} is determined automatically by IVAS in the decomposition analysis and it depends on the charge state ratio (CSR) of the O^+ (16 Da) and O_2^{++} (32 Da) peaks in the mass spectrum, which is discussed with more detail in Section 3.3. The peak-to-background ratio for the 78 Da peak was at least 1000:1 and a global time-of-flight based background correction algorithm was chosen, which is built into the analysis software.

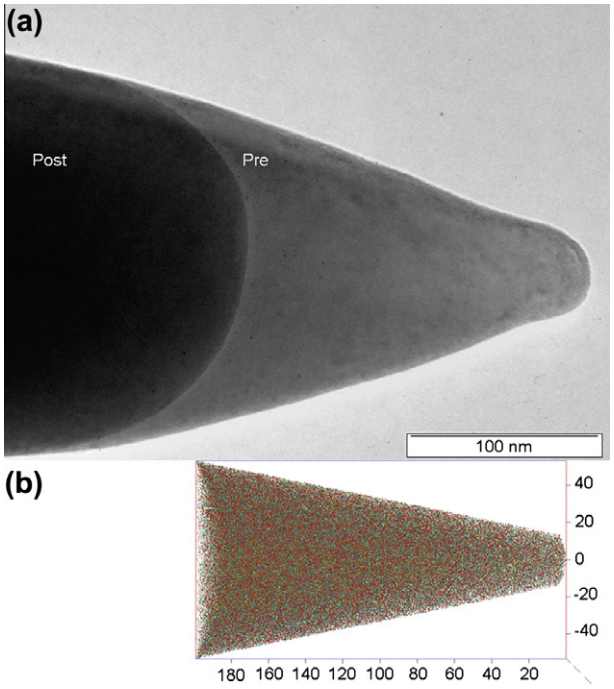

Fig. 1. (a) Overlay of two transmission electron micrographs of a representative cerium oxide atom probe specimen shown pre- and post-atom probe field evaporation, and (b) the corresponding reconstruction from the atom probe data shown at the same scale.

Atom probe data reconstruction was performed from the TEM micrographs using the "tip profile" function in IVAS, where a TEM image of the needle shape specimens is loaded on the software and the analysis volume is reconstructed according to the shape of the tip (radius increase with shank angle). Un-ranged events are not included in the reconstruction.

3. Results and discussion

3.1. Laser energy and temperature effects on mass resolving power

A representative mass spectrum of the bulk cerium oxide is shown in Fig. 2 and was obtained using a base temperature of 20 K and 1 pJ laser pulse energy; the most abundant ions and clusters observed during the analysis have been labeled. The presence of hafnium oxide (HfO_2, HfO) was also observed at concentrations below 1 at.%; it should be noted that hafnium is commonly present as an impurity in cerium oxide so low concentration of the element is not unexpected.

The effect of laser pulse energy on the mass spectra of cerium oxide is shown for comparison in Fig. 3; the spectra was acquired at 20 K for the specimen base temperature and varying the laser pulse energy between 1 pJ and 1000 pJ. The intensity of the peaks in the mass spectra has been normalized to the CeO^{++} peak (78 Da) in all the conditions except for the run performed using 1000 pJ laser energy, which is normalized with respect to the CeO^+ peak (156 Da). The effect of laser pulse energy on the charge state ratio