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Technical Note

Application of Laser Ablation Inductively Coupled Plasma Mass Spectrometry for Characterization of U-7Mo/Al-5Si Dispersion Fuels

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ABSTRACT

This technical note demonstrates the feasibility of using laser ablation inductively coupled plasma mass spectrometry for the characterization of U–7Mo/Al–5Si dispersion fuel. Our measurements show 5.0% Relative Standard Deviation (RSD) for the reproducibility of measured $^{98}Mo/^{238}U$ ratios in fuel particles from spot analysis, and 3.4% RSD for $^{98}Mo/^{238}U$ ratios in a NIST-SRM 612 glass standard. Line scanning allows for the distinction of U–7Mo fuel particles from the Al–5Si matrix. Each mass spectrum peak indicates the presence of U–7Mo fuel particles, and the time width of each peak corresponds to the size of that fuel particle. The size of the fuel particles is estimated from the time width of the mass spectrum peak for ^{98}Mo by considering the scan rate used during the line scan. This preliminary application clearly demonstrates that laser ablation inductively coupled plasma mass spectrometry can directly identify isotope ratios and sizes of the fuel particles in U–Mo/Al dispersion fuel. Once optimized further, this instrument will be a powerful tool for investigating irradiated dispersion fuels in terms of fission product distributions in fuel matrices, and the changes in fuel particle size or shape after irradiation.

1. Introduction

Dispersion fuels such as U–Mo particles dispersed in an Al base matrix (U–Mo/Al) have been developed in order to replace highly enriched uranium fuels in research and test reactors with low enriched uranium fuels [1–4]. The Reduced Enrichment for Research and Test Reactors program, related to the US Global Threat Reduction Initiative Conversion program, support the development of low enriched uranium dispersion fuels with high uranium density for nuclear

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nonproliferation. U–Mo alloys are a potential fuel for such research and test reactors because they have an excellent irradiation performance with good stability and higher uranium density than current fuels such as U–Si, U–Zr, and U–Nd [5–7]. U–Mo fuel powders have been fabricated in the past using a centrifugal atomized method [7–9], which produces spherical particles that allow for higher fuel loading. After irradiation of U–Mo/Al fuel, however, several performance-related issues arise, such as fuel particle swelling caused by fission products, volume expansion by interaction layer (IL) growth, and large pore formation at the IL–Al interface [10].

Accurate, rapid, and quantitative measurement of U–Mo fuels, such as the measurement of uranium isotope to qualify the low enriched uranium requirement [11], is desired by many researchers. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has been successfully applied to determine trace elements and isotope ratios in the fields of geology, materials science, and environmental science, as well as in radioanalytical and nuclear chemistry [12–16]. Compared with other techniques, LA-ICP-MS offers simpler sample preparation and higher sensitive chemical analysis down to ppb level. Electron-probe microanalysis with energy dispersive spectrometer or wave-length dispersive spectrometry has high spatial resolution, but it does not provide isotopic information. Secondary ion mass spectrometry has high sensitivity and accurate isotopic measurements, but it is expensive. LA-ICP-MS could give isotope mapping from bulk analysis with a typical laser spot size and microanalysis with the laser spot size as small as a few microns. Recently, femtosecond LA-ICP-MS was used to directly measure the uranium isotopic ratio in U–10Mo fuel foils [17]. In our previous studies [18–20], the isotropic ratios of elements and the distribution of fission products including molybdenum in spent nuclear fuel were successfully measured by shielded LA-ICP-MS with simple sample preparation. At present, our interest is in the application of LA-ICP-MS for the analysis of U–Mo/Al dispersion fuel after irradiation, where we seek to determine the distribution of isotopes in the fuel matrix and the dispersed domain of each isotope. The swelling of fuel particles by fission products and volume expansion by IL growth can both affect the dispersed domain of each isotope and the size of fuel particles. Prior to applying this technique to directly examine irradiated U–Mo/Al dispersion fuel, preliminary LA-ICP-MS tests of unirradiated U–Mo/Al fuel are necessary to confirm the capabilities of this instrument.

This technical note aims to evaluate the feasibility of applying LA-ICP-MS for the characterization of U–7Mo/Al–5Si dispersion fuel before irradiation. To achieve this purpose, LA-ICP-MS is performed to measure the size of U–7Mo fuel particles as well as the reproducibility of $^{98}Mo/^{238}U$ ratios in NIST-SRM 612 glass and U–7Mo fuel particles.

2. Materials and methods

U–7Mo/Al–5Si dispersion fuel was prepared through a centrifugal atomization process at the Korea Atomic Energy Research Institute, Daejeon, Korea. The fuel plate with cladding was cut to a length of 28 mm and thickness of 1.4 mm, and embedded in the resin for measurement as shown in Fig. 1. The fuel meat composed of the mixture zone of U–7Mo particles and Al–5Si matrix is distinct from the cladding region. The fabricated U–7Mo particles are spherical (10–90 μm in diameter) within the Al–5Si matrix. NIST-SRM 612 glass, a universal standard for laser ablation applications, was also studied to evaluate the capability of our laser ablation setup. NIST-SRM 612 is a glass wafer that includes 61 trace elements to facilitate development of chemical analysis. Among them, mass fractions of 15 elements are certified by National Institute of Standards and Technology (NIST). Isotopes ^{98}Mo and ^{238}U were selected as reference isotopes to evaluate the reproducibility of the measured $^{98}Mo/^{238}U$ ratios in the dispersion particles of the U–7Mo/Al–5Si fuel matrix and NIST-SRM 612 glass; ^{98}Mo and ^{238}U are the main isotopes of Mo and U in a U–7Mo particle. The reproducibility of the measured $^{98}Mo/^{238}U$ ratios indirectly represents the uniformity of Mo/U element ratio that could confirm the composition of a U–7Mo particle.

Measurements were performed by ICP-MS (Element; Thermo Scientific, Bremen, Germany) coupled to a laser ablation system (LSX-213; Teledyne CETAC Technologies,

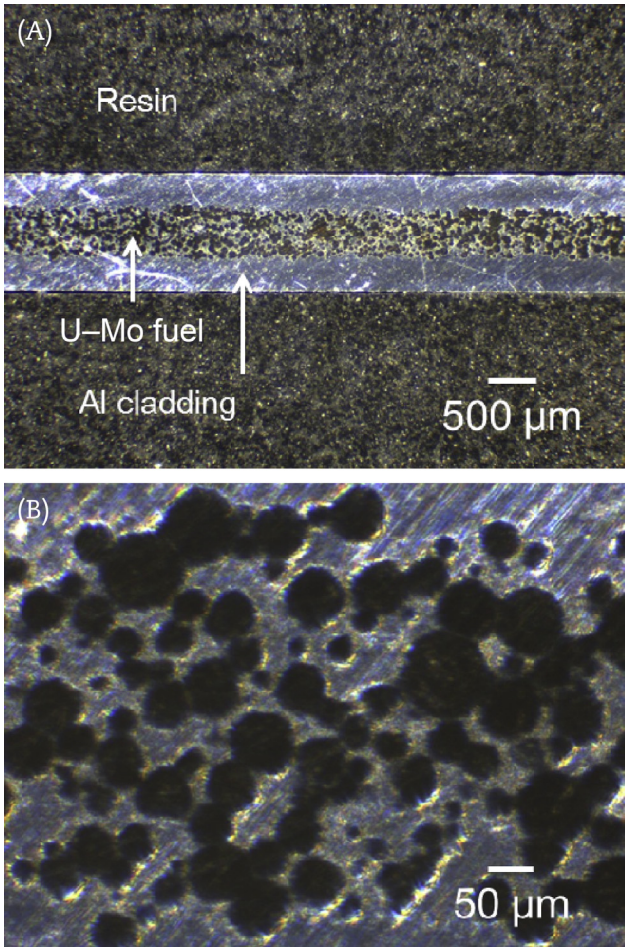

Fig. 1 – Fuel plate with cladding cut and embedded in the resin for measurement. (A) Cross section of U–7Mo/Al–5Si fuel embedded in resin. (B) U–7Mo/Al–5Si fuel meat composed of U–7Mo particles dispersed in the Al–5Si matrix.

Omaha, NE, USA). The ablation chamber is a 50 mm diameter × 50 mm high cylindrical designed standard cell. This offers washout of three orders in an average of just 2–3 seconds, independent of the ablation position inside the cell. The ablated materials by a wavelength of 213 nm with pulse duration of < 5 nanoseconds were introduced into the ICP torch with helium carrier gas (250 mL/min) and argon sampling gas (700 mL/min). The ablated materials were ionized through the plasma operated at 1,300 W radiofrequency power, and then the ions entered the mass detector. For this work, the ICP-MS system (Thermo Scientific) was optimized at the maximum ion intensity for ^{238}U in standard solutions. The detailed ablation conditions and analysis parameters of the samples are listed in Table 1.

Spot analysis and line scanning were used for LA-ICP-MS measurements. Spot analysis allows for the selection of individual ablation spots on a sample with specific laser spot sizes, while line scanning allows the laser to move at a set scan rate in a straight line across the sample.

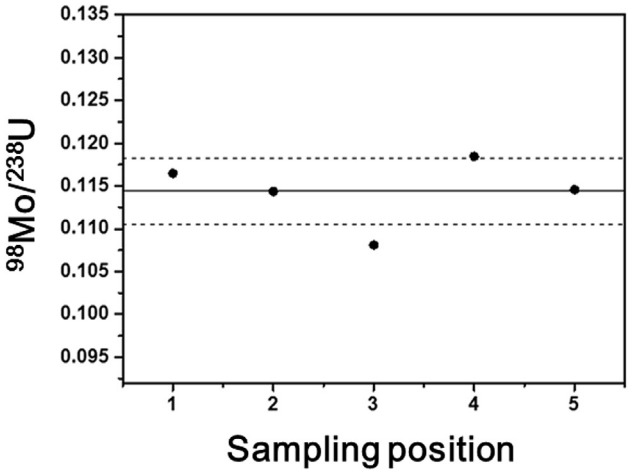

Fig. 2 – The $^{98}Mo/^{238}U$ ratios of NIST-SRM 612 glass. Average $^{98}Mo/^{238}U$ ratios (line), 1 standard deviation (dashed line), and % RSD values are 0.114 4, 0.003 9, and 3.4, respectively.

3. Results and discussion

Spot analysis with a 20-second shutter delay was used to confirm the reproducibility of the measured composition ratios for both ^{98}Mo and ^{238}U in the NIST-SRM 612 glass and in the fuel sample measured by LA-ICP-MS. Fig. 2 shows the $^{98}Mo/^{238}U$ ratios with 3.4% RSD from the spot analysis of the NIST-SRM 612 glass, which indicates a homogeneous elemental distribution on the glass; these results support the reproducibility of the LA-ICP-MS measurements. The size and energy density of the laser were optimized by confirming the intensity and width of the mass spectrum peak for the NIST-SRM 612 glass. However, different laser ablation parameters were used for the fuel sample. The spot size, energy density, pulse frequency, and number of shots per point for laser ablation of the U–7Mo particles are all lower than those in the case of NIST-SRM 612 glass ablation, as the average diameter of the fuel particles is smaller than 100 μm and the laser ablation efficiency of the fuel samples under identical conditions saturates the ^{238}U signal.

We ablated 25 sampling points on the U–7Mo particles in the fuel sample to confirm the stability of the LA-ICP-MS measurement. The $^{98}Mo/^{238}U$ ratios for each measurement from spot analysis are plotted in Fig. 3. Individual $^{98}Mo/^{238}U$ ratios show a variation in the elemental distribution within the U–7Mo particles. The measured $^{98}Mo/^{238}U$ ratios with 5.0% RSD indicate good reproducibility for the Mo and U in the U–7Mo particles, similar to the case of the NIST-SRM 612 glass despite some minor variations. In the other result, the isotopic ratio of $^{235}U/^{238}U$ from five successive passes over a single line scan in the U–10Mo sample with a femtosecond LA-ICP-MS setup had 3% RSD [17]. This reproducibility of the measured data by LA-ICP-MS supports the notion that our instrumentation can provide precise isotope ratio measurements for fuel samples. The molar ratio between ^{98}Mo and ^{238}U calculated from molar weight ratio of U–7wt%Mo is 0.056 15. The measured $^{98}Mo/^{238}U$ ratio is less than this calculated molar ratio because the measured value did not consider any mass bias corrections. ICP-MS instrumentation has variable sensitivity across the atomic mass range [21]. Plasma shielding- and matrix-dependent effects could affect the measurement. A small plasma potential may exist due to incomplete shielding of the ICP and could affect the ionization efficiency of each element. The matrix of the sample could affect the

Table 1 – Operating conditions and measurement parameters for LA and ICP-MS.

LA parameters	LSX-213 (Teledyne CETAC Technologies)	
Sample	U–7Mo/Al–5Si fuel	NIST-SRM 612 glass
Laser (Nd:YAG) wavelength (nm)	213	
Pulse width (nsec)	<5	
Energy density (J/cm^2)	55	100
Spot size (μm)	20	100
Pulse frequency (Hz)	10	20
Number of shots per point	30	100
Ablation type	Spot analysis & line scan	Spot analysis
Carrier gas flow (He) (mL/min)	250	
ICP-MS conditions	**Element (Thermo Scientific)**	
Cooling gas flow (mL/min)	1,600	
Auxiliary gas flow (mL/min)	700	
Sampling gas flow (mL/min)	700	
Radio frequency power (W)	1,300	
Resolution mode	Low	
Isotopes	^{98}Mo, ^{238}U	
Acquisition mode	E-scan	
Samples per peak	30	
Sample time (sec)	0.0100	
Mass window (%)	150	
Search window (%)	150	
Integration window (%)	50	

ICP-MS, inductively coupled plasma mass spectrometry; LA, laser ablation.

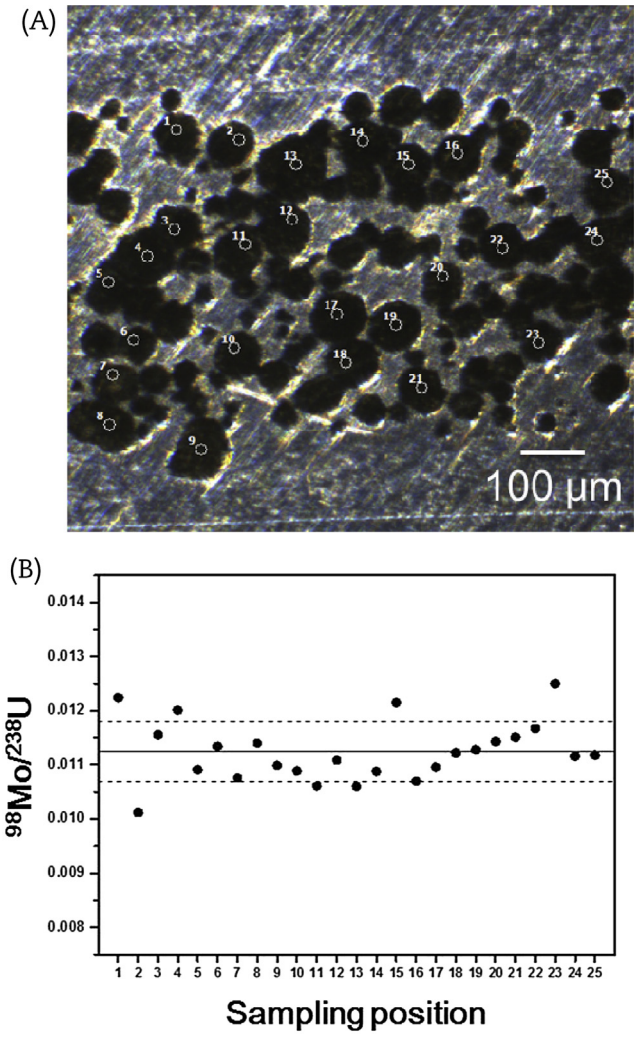

Fig. 3 – The ^{98}Mo/^{238}U ratios for measurements from spot analysis. (A) Sampling positions, using a 20 μm ablation spot size for spot scanning on U–7Mo particles in U–7Mo/Al–5Si fuel meat. (B) The ^{98}Mo/^{238}U ratios of U–7Mo particles. Average ^{98}Mo/^{238}U ratios (line), 1 standard deviation (dashed line), and % RSD values are 0.011 25, 0.000 56, and 5.0, respectively.

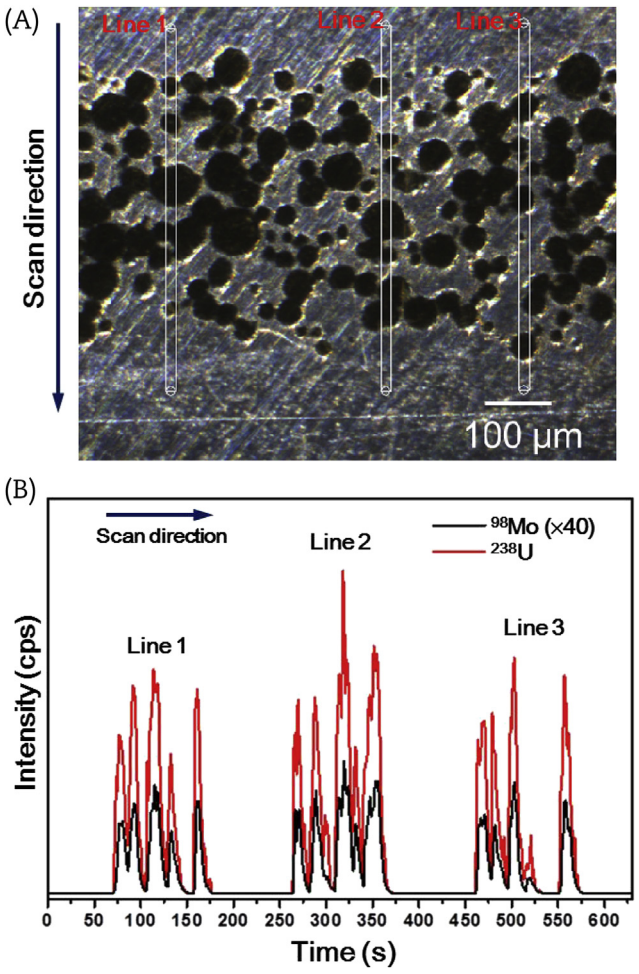

Fig. 4 – Line scanning. (A) Laser ablation lines of fuel meat and cladding with scan direction. (B) Laser ablation mass spectra of ^{98}Mo and ^{238}U from line scans with a 5 μm/s scan rate. The average ^{98}Mo/^{238}U ratio for line scans is 0.010 64 based on the peak area analysis used in spot analysis.

amount of ablated material per pulse. Future experiments will be designed to evaluate the accuracy of the quantitative element ratios with corrections for the ionization efficiency of each element. It is expected that the ratio of the fission products in irradiated U–Mo/Al fuel will be measured by LA-ICP-MS with accuracy and precision after perfect optimization and correction.

Three line scans were set to confirm the ability of our instrument to distinguish fuel particles from the Al–5Si matrix in line and to determine the size of the U–7Mo particles. Fig. 4 shows laser ablation lines 1, 2, and 3 on the samples, including the fuel meat and cladding region. Each line scan goes across the fuel sample from top to bottom at a scan rate of 5 μm/s. The mass spectrum signals of the ^{98}Mo and ^{238}U isotopes from the line scans are also shown in Fig. 4. Apparent features of the ^{98}Mo and ^{238}U mass spectra show nearly identical responses to one another, and both can distinguish U–7Mo fuel particles from the Al–5Si matrix. The average ^{98}Mo/^{238}U ratio for line scans is 0.010 64 based on peak area analysis used in spot analysis. This value is quite similar to that from spot analysis. Each peak indicates the presence of U–7Mo fuel particles along the corresponding laser ablation line, while the time width of the peak corresponds to the size of the fuel particle. The ^{98}Mo and ^{238}U isotope signals exclusively appear in the U–7Mo particle regions rather than the Al–5Si matrix and cladding regions. This indicates that U–7Mo particles are well dispersed within the Al–5Si matrix without experiencing breakdown.

The correlation of the scan rate with the line scan distance from LA-ICP-MS could enable the measurement of dispersed domain of ^{98}Mo corresponding to U–7Mo particle size. In Fig. 5, point A of the U–7Mo particle (~25 μm diameter) corresponds to the ^{98}Mo peak with a time width of ~20 seconds. First, the tailing time width of ~6 seconds corresponding to the right side of the peak in the mass spectrum must be considered when evaluating the fuel particle size. This tailing is

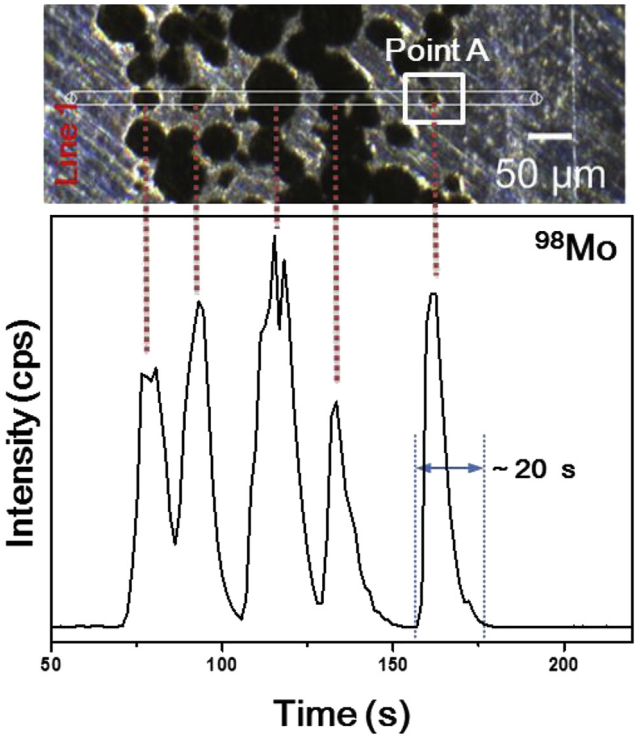

Fig. 5 – Laser ablation line of fuel meat and cladding and laser ablation mass spectrum of ^{98}Mo. Point A (~25 μm diameter) has a time width of 20 seconds during line scanning with a 5 μm/s scan rate.

mainly due to the slow helium carrier gas flow and the distance it travels in the tubing (5 m); longer sample tubing from laser ablation setup induces higher signal dispersion and requires longer washout times [16]. By subtracting the tailing time width from the whole scan interval at point A, the practical scan time here is estimated to be 14 seconds. Considering the laser spot size of 20 μm and scan rate of 5 μm/s, during the first 4 seconds and last 4 seconds of the scan interval, the laser spot is not precisely located within point A. At that time, the laser spot partially overlaps with point A. The time interval of total overlap between the laser spot and the area of point A during line scanning is 6 seconds. The diameter of point A, therefore, is calculated to be 30 μm based on a scan rate of 5 μm/s and an actual scan interval of 6. This closely matches the optically measured diameter of point A. This measuring process shows the capability of LA-ICP-MS to determine the dispersed domain of ^{98}Mo corresponding to the fuel particle size. This could further be applicable to measuring the change of fuel particle sizes caused by volume expansion by IL growth and swelling by fission products during irradiation of U–Mo/Al dispersion fuels. After further process optimization, such as shortening of sample line from laser ablation setup to ICP-MS in order to remove the dispersed tailing in the mass spectrum, this instrument should successfully measure the isotope ratios and size differences of the dispersed domain of isotopes in irradiated U–Mo/Al dispersion fuels. LA-ICP-MS could measure the line profiles and domains of fission products in irradiated U–Mo/Al dispersion fuels. Such line profiles and domains of isotopes will represent how fission products are distributed and migrated in fuel meat, and which fission products widely diffuse from the fuel particles. This information would be very useful in identifying the performance and characteristics of irradiated U–Mo/Al dispersion fuels.

4. Conclusion

In summary, we examined the feasibility of LA-ICP-MS for characterizing U–7Mo/Al–5Si dispersion fuels. The ^{98}Mo/^{238}U ratios measured in each U–7Mo particle by LA-ICP-MS are reproducible with 5.0% RSD. In addition ^{98}Mo/^{238}U ratios of NIST-SRM measured in this manner have results of 3.4% RSD values. These results support the reliability of our LA-ICP-MS measurements. The reproducibility of the measured data also supports the capability of our instrumentation for precise isotope ratio measurements in fuel samples. The ability of this setup to distinguish the fuel particles from the Al–5Si matrix was also confirmed. Each peak in the mass spectra of three laser ablation line scans indicates the presence and positions of U–7Mo fuel particles along the scanned line. The ^{98}Mo and ^{238}U isotope signals appear only in U–7Mo particle regions, and not on the Al–5Si matrix and cladding. The time width of each peak in these mass spectra corresponds to the size of the fuel particle, which is estimated from the ^{98}Mo mass spectrum from LA-ICP-MS and the scan rate used for that line scan. This measuring process fully demonstrates the capability of LA-ICP-MS to determine the domain of ^{98}Mo corresponding to fuel particle size. The preliminary studies in this technical note clearly demonstrate that LA-ICP-MS has the potential to directly identify isotope ratios and dispersed domain of isotopes in U–Mo/Al dispersion fuels, and further optimization will only serve to expand the capabilities of this technique. Overall, LA-ICP-MS will provide useful information regarding the performance and characteristics of irradiated U–Mo/Al dispersion fuels.

Conflicts of interest

No conflict of interest.

Acknowledgments

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