Overview of CETAMA Activities and Assessment of U and Pu Quality Analysis Results

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Abstract

CETAMA, the analytical methods committee of the French atomic energy commission, is a link between analysts from different laboratories working in nuclear fields. Its main mission is to improve the quality of measurement and analysis results by proposing suitable scientific and technical developments:

- Fabrication, certification and supply of certified reference materials
  - 35 products currently listed: U, Pu, Np
- Organization and interpretation of inter-laboratory comparisons for Quality Assessment of Analytical Results or for validation of analysis methods
  - For example: U or Pu proficiency tests
- Writing methods and reference documents validated by laboratory experience
  - For example: Gamma spectrometry applied to waste characterization
- Organization of workshops to promote the reporting of experience among analysts.
  - Seminars on “sampling” in 2005 and “methods validation in 2006

CETAMA has constituted a “competency network” organized into working groups that pool their knowledge on fuel cycle (U,Pu) analysis, waste characterization and environmental measurements. Nearly 300 nuclear analysts, engineers and technicians are in this network, as illustrated here by a discussion of the organization of intercomparisons on U or Pu analysis.

For about 40 years, Laboratories from CEA Nuclear Energy Division and AREVA group have been the main stakeholders in CETAMA activities. More recently, we have enhanced international collaboration with analytical groups from IAEA, EURATOM ABBAC, etc. In order to extend the network, we wish to share analysis skills with other European teams.

Keywords: analytical techniques, interlaboratory comparisons, reference materials

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1 INTRODUCTION

Ensuring reliable and accurate measurements of materials has long been a major issue in nuclear activities, whether in support of research, for process control, or environmental protection by monitoring releases. The analytic approaches are validated by demonstrating that they are suitable for their intended objectives and meet the particular requirements of each unit. In this respect, CETAMA contributes to improving the quality of measurement and analysis results for both nuclear and non-nuclear applications.

Its core activity involves the coordination of working groups with members from laboratories specialized in a given field to compile a referential and methods knowledge base and to provide laboratories with measurement standards. Through the interlaboratory comparison programs that it organizes and through the reference materials it supplies, CETAMA helps consolidate the scientific expertise of the participating laboratories and provides them with the means for regularly assessing their analytic performance.

2 GENERAL OVERVIEW OF THE CETAMA

The main missions of the CEA's *Commission d'Établissement des Méthodes d'Analyse* (CETAMA: committee for the establishment of analysis methods) have been regularly confirmed since its creation in 1961, and are organized around four main activities:

- certifying, and providing reference materials for analyses of nuclear materials (uranium, plutonium etc.);
- organizing and interpreting the results of inter-laboratory round-robin analysis comparisons;
- writing methods and technical documents;
- promoting the reporting of experience and dissemination of scientific information.

CETAMA is structured as a network of expertise organized into topical working groups and coordinated by an operational team of four persons.

Participants in the working groups come mainly from the CEA and AREVA and more recently from IRSN and EDF labs, as well as some university laboratories. They are above all specialists in a given field, participating in a program to share knowledge among all the members. About fifteen groups are currently active, comprising some 300 persons from 80 different laboratories.

The analytical skills arising from the pooled knowledge and expertise of all the laboratories participating with CETAMA are disseminated by organizing specialized seminars combining a review of the lessons learned from experience with training programs that contribute to the deployment of metrological methodology.

With its network of partner laboratories, CETAMA synthesizes, certifies and sells reference materials, mainly containing uranium and plutonium. In addition to meeting the needs of the CEA labs, they are distributed principally to nuclear industrial labs (AREVA, EURATOM, JNFL), to inspection agencies (IAEA), and to international metrology institutes (IRMM, ITU).

Among the active working groups, some are concerned more specifically with assaying substances in matrices: uranium, plutonium, water. Others are concerned more with analyzing radionuclides in waste materials, waste packages, or the environment, or for clearly identified program support purposes such as reprocessing solvents and degradation products, dismantling of nuclear facilities, or speciation studies. Certain groups are dedicated to instrumental techniques: atomic emission and absorption spectrometry (ICP–AES), mass spectrometry (ICP–MS or TIMS), nondestructive radiological analysis of waste packages, surface analysis, or chromatography. From the broad range of our activities we have chosen to describe in greater detail the U/Pu round robin in links with U/Pu reference materials.

3 ASSESSMENT OF THE QUALITY OF U AND PU ANALYSIS RESULTS IN THE NUCLEAR INDUSTRY

3.1 GENERAL APPROACH

For many years CETAMA has organized three types of interlaboratory measurement comparisons:
- qualification tests in which laboratory test performance is assessed in an interlaboratory round robin,
- method validation programs in which the use of a particular measurement method is required,
- accurate characterization of nuclear materials (U, Pu, Np) for certification and use as reference materials (RMs)

RMs can be used:
- to adjust, calibrate or evaluate analytical methods,
- to establish calibration curves during equipment setup procedures,
- to prepare secondary reference materials,
- to recalibrate analytical methods and instruments at periodic intervals.

CETAMA can supply RM products to meet the objectives and requirements of the nuclear industry: increasing analytical accuracy, new materials requiring analysis, new specifications to be confirmed, and replacement of RMs that are nearly out of stock. In the current catalog (35 products), RMs are mainly U or Pu materials with certified major element concentrations or U with specified impurities concentration.

Figure 1. Plutonium metal reference materials (MP2).

3.2 EQRAIN URANIUM AND PLUTONIUM ROUND-ROBINS

Since 1987, the “EQRAIN” program, as it is known from the French acronym for “Quality Assessment of Analysis Results in the Nuclear Industry”, has regularly organized interlaboratory comparisons concerning the elemental analysis of uranyl nitrate solutions (EQRAIN U) and plutonium nitrate solutions (EQRAIN Pu). These comparisons provide the laboratories with an opportunity to assess their performance in relation with their needs, to comply with normative requirements, to check for possible deviations and to implement the necessary corrective action. They also allow the participating laboratories to compare different analytical techniques and to improve their methods. The resulting data are used by the laboratories to determine their uncertainty.

Each periodically organized round-robin concerning uranium- or plutonium-based materials includes 12 to 40 participants, half of whom are from institutions outside France.

3.3 DESCRIPTION OF THE ANALYSIS SOLUTION

The samples are fabricated and packaged, and the benchmark values are determined by the nuclear materials metrology laboratory (LAMMAN) which is suitably equipped and uses methods validated for the execution and inspection of these operations. It is capable of certifying mass concentrations within 0.1% (relative). LAMMAN is situated in the Atalante complex at Marcoule.

Figure 2. Overall view of Atalante facility

The procedure adopted consists in preparing pure uranyl nitrate solutions and pure plutonium nitrate solutions by accurate weighing: about 5 $g \cdot kg^{-1}$ for plutonium, and about 250 $g \cdot kg^{-1}$ for uranium.

The uranium or plutonium concentrations of the reference solutions are verified by LAMMAN on sealed ampoules sampled at random from the batch according to a sampling plan. The deviation between the value calculated from the weighed quantities and the valued determined by measurement must not exceed 0.1% (relative).

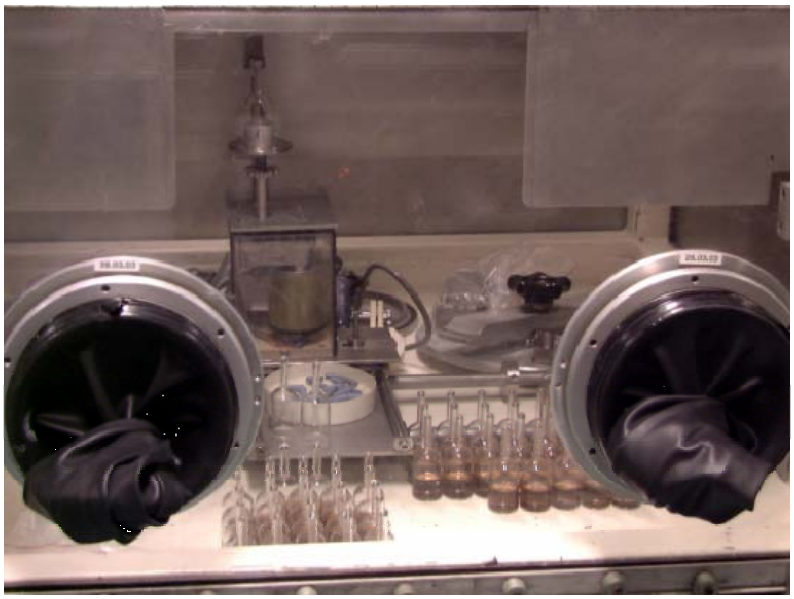

Figure 3. Ampoules of plutonium nitrate solution

3.4 ANALYSIS METHODS

The participants routinely use destructive methods (mainly potentiometry, coulometry, gravimetric analysis, etc.) and nondestructive methods (X-ray or visible emission spectrometry, etc.).

In the first category, the Davies & Gray method has been widely implemented for U for nearly 40 years and is still a reference. The inherent performance of coulometry makes it the reference method for Pu analysis after the abandonment of the MacDonald & Savage method, which is highly selective but complex.

Isotope dilution mass spectrometry (IDMS) has been used increasingly since 1997 for U and Pu. K-edge uranium or plutonium assay is applicable over a wide concentration range.

4 INTERPRETING THE U/PU EQRAIN RESULTS

4.1 METHODOLOGY ADOPTED FOR EXAMINING THE RESULTS

For each sample and each laboratory, we consider :

- the relative deviation from the benchmark value;
- an estimated standard deviation for the measurements performed by the laboratory and an indicative confidence interval;
- the number of results outside the permissible limit;
- deviations by class, for example the number of results with deviations of less than 0.1% and the number of results with deviations of less than 0.5%.

4.2 RESULTS ILLUSTRATED BY SOME EXAMPLES

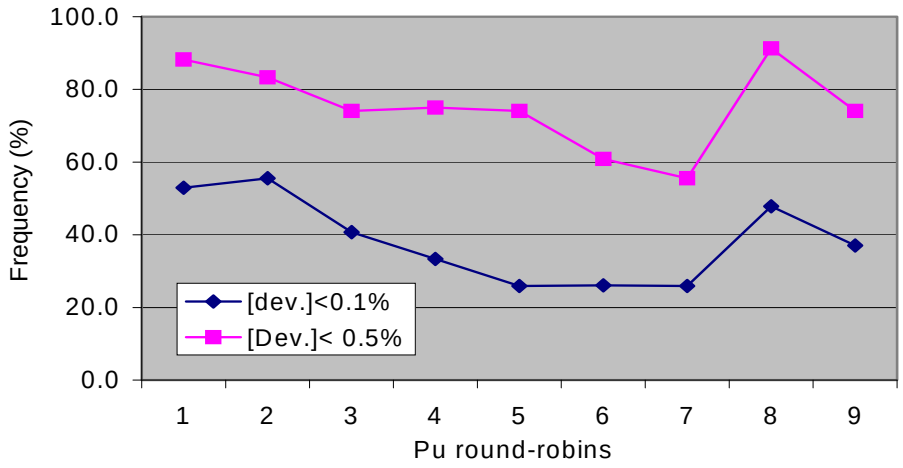

Figure 4. Comparison of results with benchmark values for plutonium round-robins

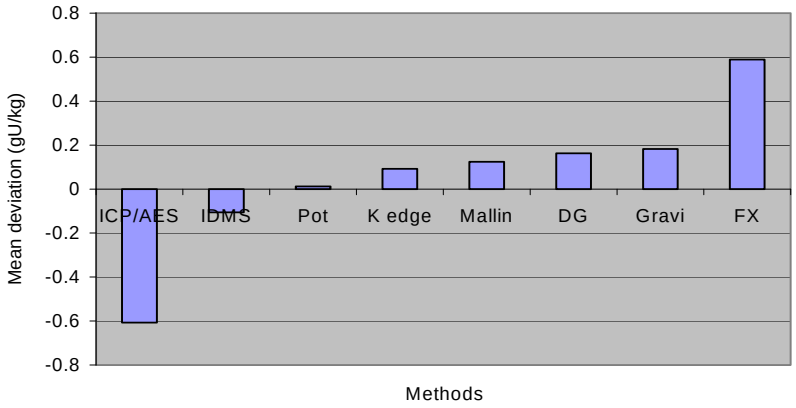

Figure 5. Trueness assessment of assay methods during EQRAIN U round-robins

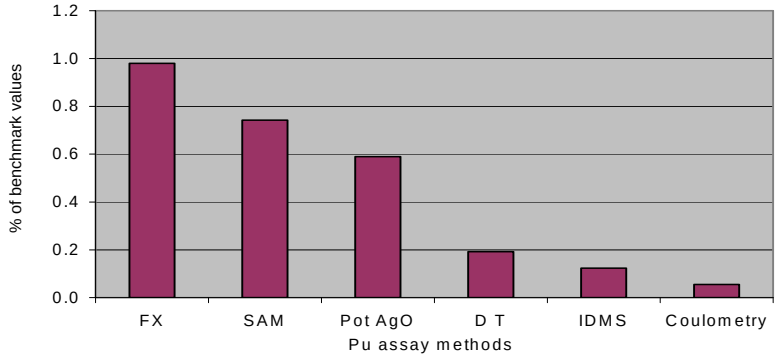

Figure 6. Reproducibility assessment of assay methods during EQRAIN Pu round-robins

5 CONCLUSIONS

Organized comparisons in the form of interlaboratory round-robins provide a solid foundation for guaranteeing analysis quality of the desired level and a firm commitment to progress. Comparative measurement programs of this type do indeed entail extra work, but they provide the laboratory with an opportunity to test and validate its methods and to identify analytical problems. More generally, they ensure the consistency of the results reported nationally and internationally and provide an opportunity for the participants to assess their analysis methods.

CETAMA encourages laboratories to participate in these round-robins, which supplement the basic work that any analysis laboratory should consider as a prerequisite for ensuring the credibility of its results.

6 RELEVANT STANDARDS

ISO/IEC Guide 43-1:1997 Ed. 2, Proficiency testing by interlaboratory comparisons – Part 1: Development and operation of proficiency testing schemes

ISO Guide 98:1995 Ed. 1, Guide to the expression of uncertainty in measurement (GUM)

ISO 13 528:2005 Ed. 1, Statistical methods for use in proficiency testing by interlaboratory comparisons

ISO 5725-1:1994 Ed. 1, Accuracy (trueness and precision) of measurement methods and results – Part 1: General principles and definitions

AFNOR FD X07-021 (October 1999) Fundamental standards – Metrology and statistical applications – Aid in the procedure for estimating and using uncertainty in measurement and test results

ISO/IEC 17 025:2005 Ed. 2, General requirements for the competence of testing and calibration laboratories

AFNOR XP T90-220 (August 2003) Protocol for estimating the uncertainty associated with an analysis result for physicochemical analysis methods

Post-irradiation-examination of irradiated fuel outside the hot cell

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Abstract
Because of their high radioactivity, irradiated fuels are commonly examined in a hot cell. However, the Idaho National Laboratory (INL) has recently investigated irradiated U-Mo-Al metallic fuel from the Reduced Enrichment for Research and Test Reactors (RERTR) project using a conventional unshielded scanning electron microscope outside a hot cell. This examination was possible because of a two-step sample-preparation approach in which a small volume of fuel was isolated in a hot cell and shielding was introduced during later stages of sample preparation. The resulting sample contained numerous sample-preparation artifacts but allowed analysis of microstructures from selected areas.

KEYWORDS: scanning electron microscopy (SEM), sample preparation, Reduced Enrichment for Research and Test Reactors (RERTR), irradiated fuel

1. Introduction
The Reduced Enrichment for Research and Test Reactors (RERTR) project is developing low-enrichment uranium (<20% U-235) fuels that can be used instead of the current high-enriched uranium fuels in research reactors. Two kinds of fuel are under development: dispersion fuels, in which the uranium is dispersed in fine particles, and monolithic fuels, in which it is a constituent of a homogeneous alloy [1].

This paper describes preparing two samples of irradiated RERTR-6 dispersion fuels for examination in a conventional (unshielded) scanning electron microscope and illustrates consequences of the sample-preparation technique for the kinds of data that can be collected from the samples.

2. Samples
Two dispersion fuel plates were prepared at the Fuels and Applied Sciences Building (FASB) at the Idaho National Laboratory (INL). Each plate had a central fuel zone approximately 0.06 cm thick, and consisting of fine particle (typically <100 μm diameter) of U-7Mo embedded in an aluminum-alloy matrix. The fuel zone was sandwiched between two layers of Alloy 6061 cladding, each 0.04 cm thick. The total nominal as-fabricated thickness of each plate was 0.14 cm.

The plates were irradiated in the Advanced Test Reactor (ATR) at the INL to an average burnup of 49-50% in the mid-plate region. Irradiation ended in November, 2005. A gamma scan performed in September, 2006, indicated that the isotopes with the highest contribution to the sample radioactivity at that time were Ce-144, Nb-95, Zr-95, Ru/Rh 106, Cs-137, Cs-134, Ru-103, and Ce-141 (listed in order of decreasing contribution to the gamma scan); however, some of the shortest-lived isotopes (particularly Nb-95) would have almost completely decayed to stable or long-lived isotopes by the time samples were prepared for microscopy in late May, 2007. Radiation readings from a punching with a nominal 1 mm diameter through the thickness of one of the plates were 300 mSv/hr combined beta-gamma and 3 mSv/hr gamma (as measured at contact with a Ludlum model R020 ion chamber detector) when the samples were prepared for SEM analysis.

Each irradiated plate was prepared for optical metallography in the hot cell by grinding it with a series of abrasives, ending with a nominal 3 μm abrasive polishing fluid. Samples were not etched before examination. Optical examination of the irradiated plates indicated that each retained its layered structure consisting of a central fuel zone with particles dispersed in a matrix, surrounded by two particle-free layers corresponding to the original cladding (Figure 1a). Higher-magnification views (Figure 1b) show that the microstructure of the fuel zone consists of particles, dispersed in a matrix. Each particle has a dark center surrounded by a lighter-colored ring. Previous analyses of similar samples (e.g., [2-6]) indicate that the rounded particles are what remains of the original U-Mo

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alloy particles, the rings around them are U-Al intermetallic reaction products formed during irradiation, and the matrix is an aluminum alloy.

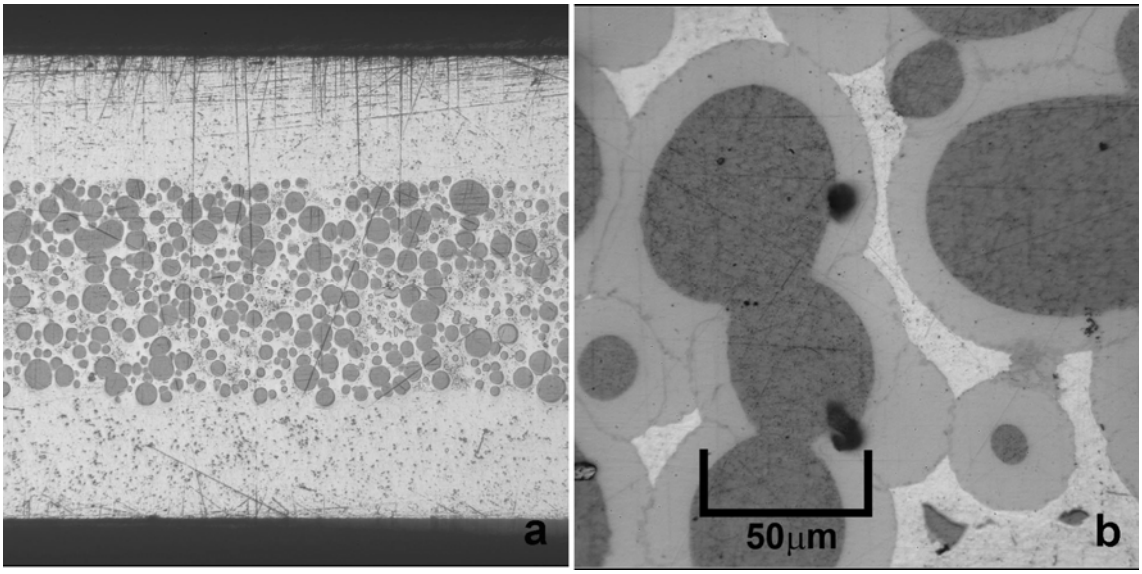

Figure 1: Optical micrographs showing typical microstructures in irradiated fuel. a) Cross-section of entire plate, showing central zone with fuel particles surrounded by particle-free zones. Total thickness of plate is approximately 0.14 cm. b) Detailed view of fuel zone.

3. Sample preparation for electron microscopy

Sample preparation for electron microscopy occurred in two steps. In the first, which was performed in the argon-atmosphere hot cell at the Hot Fuel Examination Facility (HFEF) at the Idaho National Laboratory, a commercially available press that had been modified slightly for easier operation in a hot-cell environment (Figure 2) was used to produce cylindrical punchings with nominal 1 mm diameters. Each cylinder had a nominal height of 1.4 mm (the thickness of the fuel plate). The punchings were placed in individually labeled containers and transferred into the air-atmosphere glove box at the Electron Microscopy Laboratory (EML) at the Idaho National Laboratory.

At the EML, each punching was placed on its side inside a commercially available 1.25 inch (3.175 cm) diameter, 0.75 inch (1.9 cm) tall phenolic ring that had been attached to a piece of duct tape using tweezers. A commercially available two-part epoxy that had been mixed with 325 mesh (< 44 μm) tungsten powder to provide added shielding was poured into each ring and allowed to cure at room temperature for approximately 19 hours. When the epoxy had hardened, the duct tape was removed. Each sample was manually ground using silicon carbide paper and a small amount of water to expose a longitudinal section through the fuel punching. One of the samples was initially ground with ANSI 600-grit paper (nominal abrasive size 16 μm), followed by 1200-grit (6.5 μm abrasive) paper. The other sample was initially ground with 240-grit (53 μm abrasive) paper, followed by 600-grit and 1200-grit papers. Total grinding time for each sample was 5-10 minutes.

Samples were transferred out of the glove box and decontaminated. A thin coating of sputtered Pd was applied to the surface with the exposed fuel, and the samples were transferred into the scanning electron microscope for analysis.

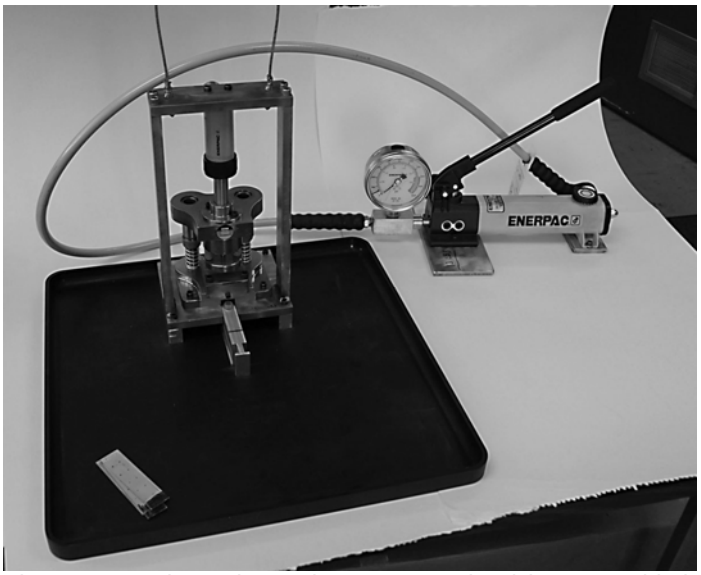

Figure 2: Punch used to make SEM samples (shown outside hot cell)

4. Results

Figure 3 shows low-magnification scanning electron microscope images of the samples. In each case, the epoxy had not completely wetted the sample, forming a bubble adjacent to the sample. As the contrast and general appearance of the sample and the tungsten-epoxy mixture are similar, these bubbles provided an easy way to locate each sample at low magnification. The tapering outline of one of the samples (Fig. 3a) suggests that the ground surface is at an angle to the long axis of the punching, while the consistent width of the other (Fig. 3b) suggests that the ground surface is approximately parallel to the long axis.

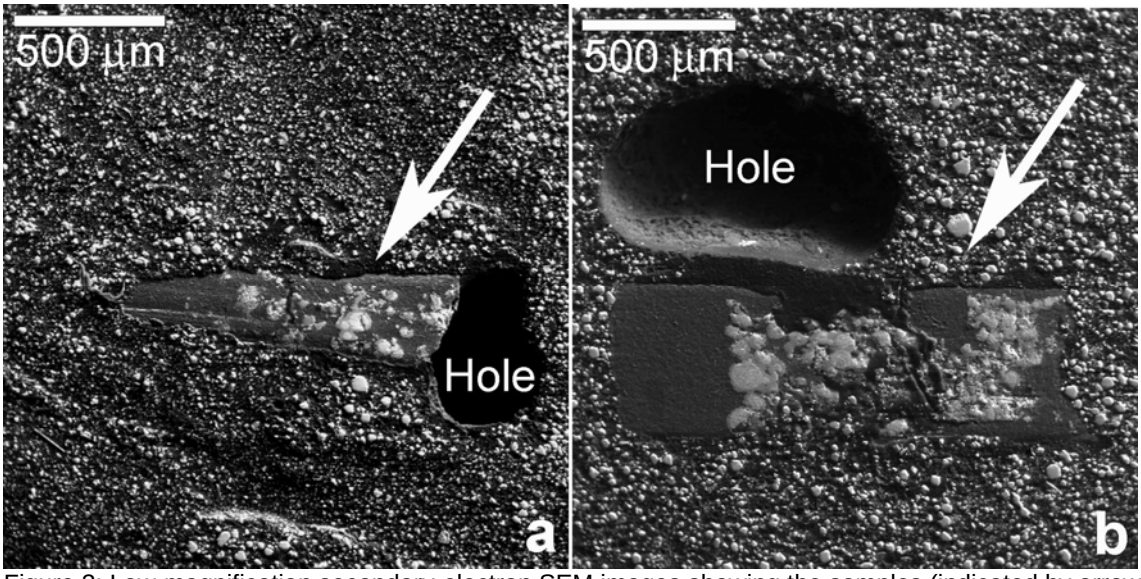

Figure 3: Low-magnification secondary-electron SEM images showing the samples (indicated by arrows) and adjacent holes. Light-colored areas in the remainder of the sample are tungsten particles embedded in the epoxy to provide shielding. a) Sample 1. b) Sample 2.

Closer inspection indicates that the samples have been strongly deformed (Fig. 4). Although the particle-free areas at the left ends of the fuel samples in Figure 3 may be cladding, the region with fuel particles extends almost to the right ends of both of the fuel samples, suggesting that the cladding at these ends of the samples

may have broken off. Sample 2 is narrower through the fuel zone than at either end (Fig. 4a), and both fuel samples show cracks extending across the punchings (Fig. 4a, b). Each sample shows regions in which sharp-edged fragments of what appear to be different materials have been jumbled together (Fig. 4c), and each shows particle-free high-Al areas along the outer edges of the punchings (Fig. 4d).

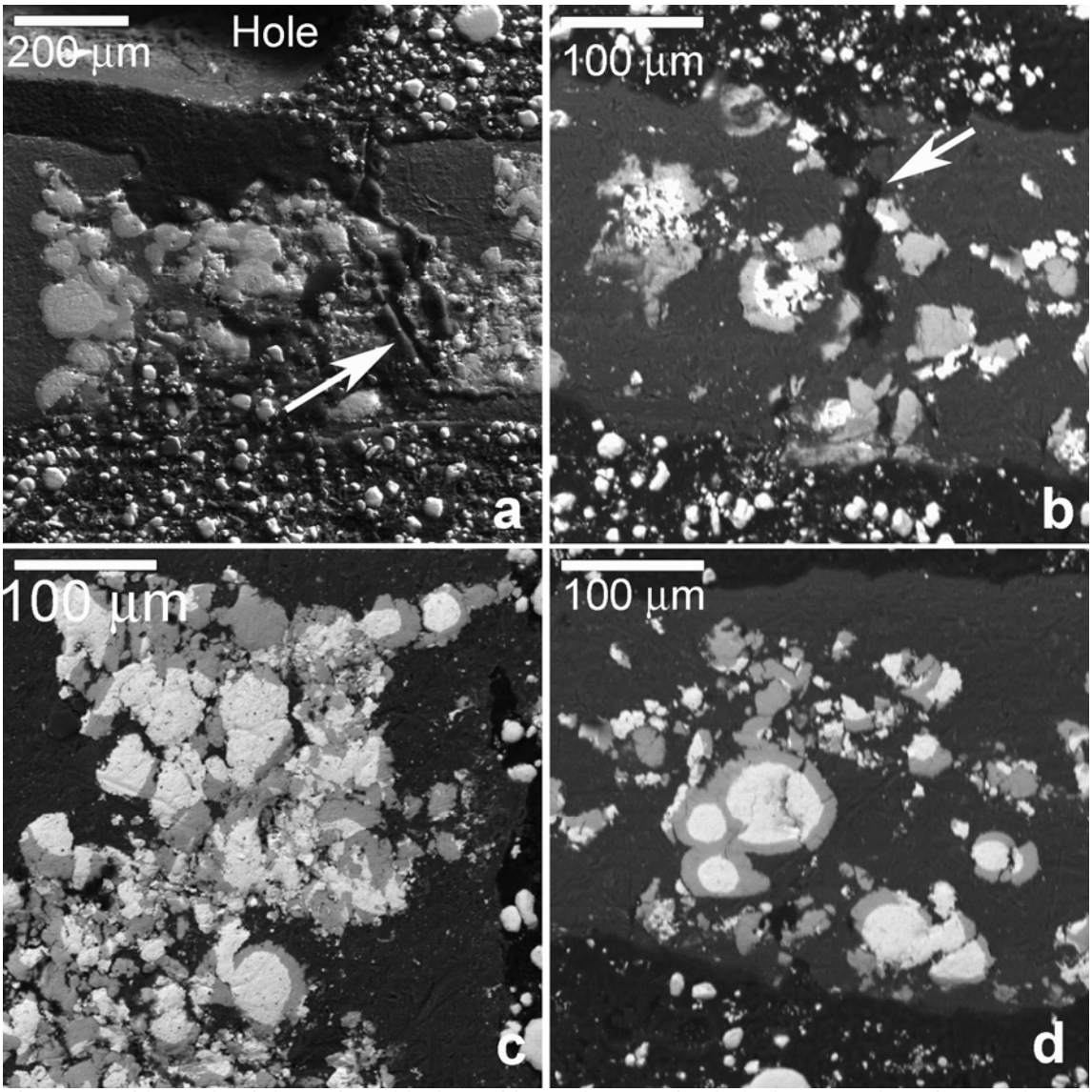

Figure 4: Evidence for deformation of fuel punchings. a) Narrowing in fuel zone and crack, Sample 2. b) Crack, Sample 1. c and d) Fuel-free zones along edges of punchings and jumbled fragments of fuel particles and reaction rims, Samples 2 and 1, respectively.

None of these characteristics would be expected from perfect cylinders taken from fuel plates with microstructures similar to those in Figure 1. However, higher-magnification images show a few particles with concentric microstructures that resemble those in the post-irradiation optical images (Fig. 5). X-ray maps confirm that the light-colored centers of these particles are high in U and Mo, the intermediate-contrast areas around the outsides are high in U and Al, and the dark colored material surrounding the particles is predominantly Al. Thus, these particles can plausibly be interpreted as representing remnants of an original fuel particle surrounded by at least the inner portion of the layer of reaction products that formed around it.

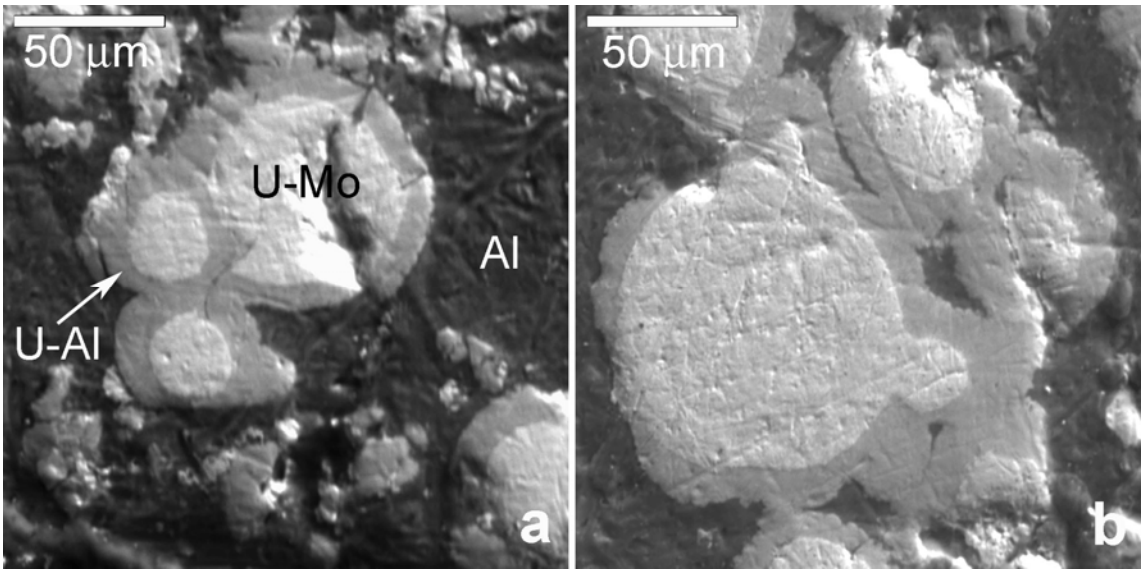

Figure 5: Secondary-electron SEM images showing microstructures similar to those in optical images. U-Mo, U-Al, and Al indicate major elements present in each area, as determined from X-ray maps. a) Sample 1. b) Sample 2.

4. Discussion

Comparisons between Figures 1, 3, 4, and 5 clearly show that the microstructure of the irradiated fuel has been changed during SEM sample preparation. Localized fractures such as those shown in Figures 3, 4a, and 4b are to be expected in brittle materials, and are unlikely to significantly affect microstructures not immediately adjacent to the fractures. However, necking of the sample in the fuel zone (Fig. 4a), particle-free areas at the edges of the punchings, and jumbled fragments (Fig. 4b-d) suggest more pervasive deformation throughout the sample, with possible flowing of the aluminum matrix. As the embedding and grinding processes used to prepare the optical and SEM samples are similar, it seems likely that the vast majority of the deformation occurred during punching.

Because of the pervasive deformation, extreme caution is necessary in interpreting data from the matrix, or data involving spatial relationships in materials in jumbled areas. Despite the pervasive deformation, it is possible to find particles whose microstructures resemble those in the optical images from the relatively intact plates. X-ray maps from these particles show chemical distributions similar to those previously reported from samples prepared with other techniques (e.g., [2-6]), and it may be appropriate to ignore the deformation of the surrounding material in interpreting data from these particles. However, data from these particles should always be compared to that obtained from samples prepared by other techniques.

Decisions about how to prepare samples and perform electron-microscope analysis of irradiated fuel necessarily involve considerations of convenience, cost, and safety. One could no doubt obtain excellent data by putting an entire cross-section of a fuel plate similar to that in Figure 1 into a scanning electron microscope. But, that would require either putting an electron microscope into a hot cell or handling relatively large volumes of fuel outside a hot cell. Both of these approaches have significant problems: putting a microscope into a hot cell leads to increased costs because of difficulty in maintaining an instrument or the need to replace it relatively frequently, while handling large volumes of fuel outside a hot cell requires great care in addressing radiation safety problems.

The approach taken here provides a compromise, in which all manipulations involving large amounts of material are performed in a hot cell, while scanning electron microscopy is perfumed outside the cell. Although the results appear promising, the data suggest that starting with slightly larger cylinders of material (e.g., a 1/16”=1.65 mm punching instead of the 1 mm used here) might produce significantly larger areas with microstructures comparable to those in optical images. Nonetheless, researchers must be constantly aware of possible deformation, particularly in the matrix where it may produce little or no direct microstructural evidence.

Comparisons between radiation readings measured on the sides of the sample with the fuel punchings and those measured in an orientation in which the tungsten-epoxy mixture was between the meter and the punchings

indicated that the tungsten-epoxy mixture reduced the beta-gamma radiation from the sample by at least two orders of magnitude.

The present data illustrates both the potential and the problems associated with samples prepared from fuel-plate punchings, and suggest that further work using larger-diameter punchings may be worthwhile. Relatively minor modifications of the techniques presented here, such as using a core drill instead of a punch, should be considered.

Acknowledgments

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