Intentional Forensics: Tagging Strategies for Rapid Nuclear Material Provenance Assessment

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Abstract

Intentional Forensics is the strategy of deliberately introducing benign and persistent material signatures during nuclear fuel fabrication and processing. The purpose is to reduce the lag time between the discovery of a "barcoded" material outside of regulatory control and the identification of its original provenance. Ensuring that individuals or organizations engaged in illicit trafficking are rapidly identified and apprehended following theft or diversion from a safeguarded facility provides a strong deterrent against unlawful activities. An integrated, multi-laboratory project in the United States is developing the scientific and technical basis that would enable voluntary adoption of this forward-looking approach to nuclear material security. Key research questions for Intentional Forensics are: What are the best strategies for intentionally tagging various nuclear materials, and where in the fuel cycle should they be introduced? How can we design taggants that provide the desired nuclear forensics outcomes while also remaining benign under reactor irradiation? How can we rapidly measure and confidently assess the information encoded in tagged nuclear material, even after it has been processed? A preliminary definition of "taggants" for this project is the use of mixtures of heteroelements, which ideally contain significant perturbations from their naturally occurring isotopic ratios, incorporated into the bulk of metallic or ceramic nuclear fuels**.** Additionally, patterned surface modifications may be employed during fabrication of higher-value, lower-throughput nuclear material, such as research reactor fuel. This presentation will give an overview of challenges in developing a taggant selection scheme that integrates probative value, manufacturability, reactor safety, and persistence in the fuel cycle. Recent experimental and modeling highlights in tagged fuel sample fabrication, irradiation, and characterization will be discussed.

Background

In the broad context of forensics, taggants are any class of materials or markers that can be applied to or incorporated within an object or material to make it identifiable. This is achieved by producing each "batch" of taggant in a unique formulation that allows a particular molecular, elemental, or isotopic composition to be registered against a specific piece of information. On a later date this composition can be analyzed in order to reveal the identity of the taggant, and thus, the object or material it is marking.

The use of deliberate taggants has been adopted within the conventional forensics community, with information encoded via physical, spectroscopic, chemical and DNA methods, and multiple commercial sources for each (Gooch, 2016). For example, recent advances in the synthesis and analysis of unique particulate features have raised the possibility of identification of materials'

provenance throughout supply chains and product life cycles. Taggant approaches have been successful for products ranging from bottled water and pharmaceuticals to electronics and narcotics. Particulate tracers of non-toxic composition that can be uniquely analyzed at part-per-billion (ppb) concentration ranges in fully automated procedures (Paunescu, 2016).

While prior investigations regarding additives to nuclear fuel have primarily been limited to efforts to impart advantageous thermomechanical or neutronic properties, the deliberate incorporation of forensic taggants into metal or oxide nuclear fuels has remained largely unexplored. Conceptual studies of nuclear fuel taggants have considered a number of options. Kristo and Lamont have considered isotopically distinct elemental taggants as candidates for introduction in conversion facilities and for rapid assessment of UO_2 fuel provenance, provided they can be added after purification of uranium ore concentrates (UOC) (Kristo, 2007; Lamont, 2006). Altered uranium isotopics (e.g. enhancement with the minor isotopes ^{234}U or ^{236}U) have the advantage of being resistant to tampering or alteration but suffer from high variability in fuel source materials. More complex taggants studied include chemical-based molecular and patterned taggants. Additionally, there have been proposals for multi-element taggants combined with perturbed isotopics, which would generate a catalogue of uniquely-ratioed elemental and isotopic "barcodes." Research and development supporting these strategies has progressed in a limited way since these proposals were offered, but this Intentional Forensics Venture project is the first concerted, multi-laboratory initiative that addresses the full lifecycle of a taggant system from synthesis and incorporation into nuclear fuels through reactor performance and reprocessing, with detection and characterization by nuclear forensics laboratories.

The purpose of this project is to identify and demonstrate taggant strategies for relevant materials, determining where in the fuel cycle they should be added for maximum benefit and how they will be isotopically, chemically, and metallurgically altered during their lifecycle in the fuel. There are a number of aspects to this work that must be considered, ranging from technical feasibility of adding a particular tag to the probative value, durability, recoverability, cost, and operational impact on producers, reactor operators, and nuclear forensics stakeholders. While our goal with this Venture is to expand what is possible by developing innovative strategies for intentional forensics, the technical and operational feasibility of an approach is also a chief consideration.

Technical Approach

The assessment of technical feasibility of nuclear fuel taggants includes several factors. Among these are the practicability of implementing the tagging strategy; for instance, some materials or approaches may have favorable attributes as a tagging strategy but would be technically impossible or impracticable. This includes materials that would have high probative value but are otherwise problematic, e.g., unique but short-lived radioisotopic tags. Technical feasibility also includes the viability of assessing provenance of a tagged material. For example, changes to a taggant through processing, and how those changes affect our ability to measure and interpret a taggant, should be predictable and limited. Finally, some taggants might prove extremely difficult to measure, or require complex purification or cutting-edge mass spectrometry approaches. While difficulty of measurement is not always a reason to eliminate a promising tag from consideration, some potential taggants might require instrument sensitivity that is unlikely to exist without major breakthroughs in mass spectrometry.

Probative Value: Evidence has probative value if it tends to prove an issue. Probative data are those that establish the existence of other facts. For a taggant to have probative value, it must contain a measurable parameter that can be readily, reliably, and repeatably recovered from various tagged materials. It is essential that the interpretation of a recovered taggant be straightforward and easily explained. A taggant that is open to ambiguous interpretation would generally be contrary to the aims of this project. An example of a highly ambiguous taggant would be an element that is also a ubiquitous but variable contaminant in nuclear fuels.

Durability: High value taggants will be those that are durable, resisting modification after being added to the nuclear fuel. Ideal taggants should be easy to introduce, yet difficult to completely separate, alter, or destroy. An analogous scenario is the odorization of hazardous gases. An ideal odorizer is highly volatile so it equilibrates quickly and evenly, readily identified by the human nose, readily associated with a gas leak, and maintains its integrity if dislocated from its point of introduction. Similar characteristics are important for taggants for nuclear fuels. Although we do not anticipate any single taggant to persist through every stage of the fuel cycle, we expect that it will be possible to design taggants that persist through at least one stage and could therefore be used to tag a specific process. One example is an isotopic taggant added to UO_2 powder after enrichment. Such a taggant could be expected to persist through pelletization, sintering, fuel rod assembly, and fuel bundle assembly. Given that finished fuel pellets are known to leave regulatory control intermittently, such a taggant could be very valuable.

Recoverability: For a taggant to provide maximum probative value, it must be easily recoverable and interpreted. It must be possible to measure and interpret the tag in a straightforward and routine fashion, unambiguously determining whether a taggant is present or absent in a given material, and then further determining the precise identity of that specific taggant. In order to do so, the taggant must be distinctive from other compounds that are fortuitously present. For example, distinguishing between a U fuel that has been deliberately tagged with Mo, and a fuel that has been deliberately alloyed with Mo, is a critical aspect of recoverability. Techniques for recovering taggant information with high fidelity to the original taggant design are needed, in order to preserve the probative value of the deliberately introduced material.

Effect on fuel performance: Among the various criteria for potential taggants, perhaps the most critical factor for widespread implementation is to minimize the taggant's effect on the fuel's performance in a reactor. Safety considerations demand that any fuel additive be completely benign in a reactor under both normal and off-normal operating conditions, and efficiency considerations require that it have minimal impact on fuel life expectancy. Ideally, taggants can be identified that are not only benign, but actually beneficial to fuel performance (e.g., reducing fuel-cladding chemical interactions), while serving a dual purpose of facilitating provenance assessment. We address this consideration in the Venture project through extensive irradiation modeling focusing on nuclear data sensitivity, neutronic effects, and thermo-mechanical effects, followed later by irradiation and post-irradiation examination of candidate materials.

Cost to Implement: Although not the primary concern for the scientific goals of this Venture, the cost of implementation receives consideration in this effort. While technological advances may allow us to overcome some analytical approaches that are currently cost prohibitive, other methods of tagging may never scale to production levels or may involve taggant materials that are simply too expensive to incorporate (e.g. exotic stable isotopes that are produced in very limited quantities). In the course of our investigations supporting this venture, therefore we will consider

both current and emerging technologies, and place some consideration on the cost to implement any tagging strategy.

Methods and Results

Bulk Taggants for Uranium Oxide Fuels: Nuclear fuels containing uranium oxide and mixed U-Pu oxide comprise the largest group of materials used in civilian power reactors for the foreseeable future. The high production throughput for oxide fuels necessitates a bulk tagging strategy that occurs just prior to fuel pellet production (Figure 1). A leading concept in the Intentional Forensics project is to develop taggant mixtures that contain perturbed stable isotopes of non-fuel elements. A suitable taggant element for this strategy will possess at least two stable isotopes (preferably more) and will be stable and non-volatile during pellet sintering processes. Unique taggant formulations can be prepared by varying the isotopic ratios as well as the element ratios. Importantly, variable isotopic ratios can retain their probative value through some instances of reprocessing, as long as the nuclear data for each isotope is sufficiently well-understood to support reconstruction of the original taggant formula. This is a unique trait of isotopically-perturbed taggants.

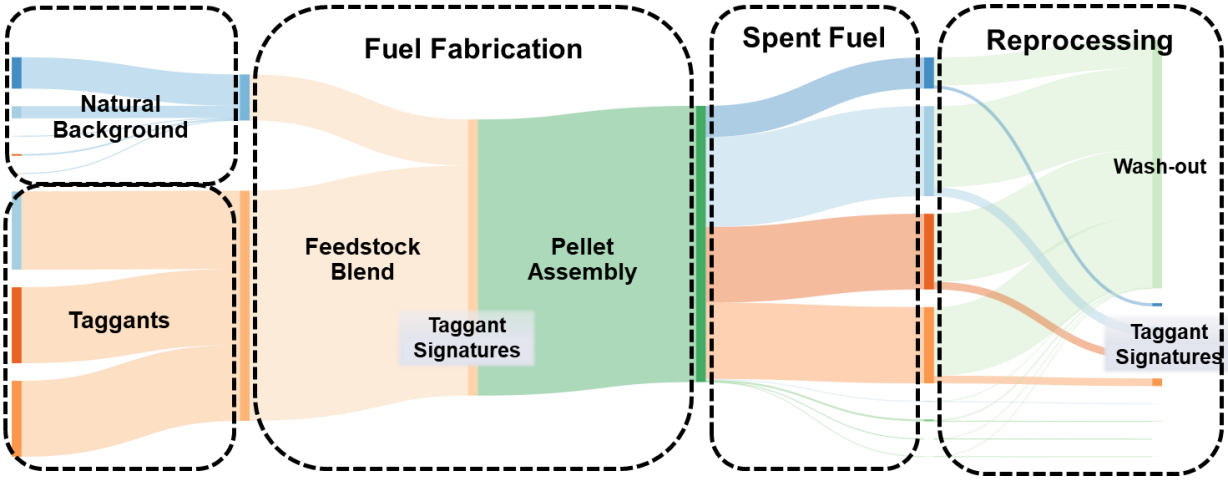

Figure 1. Hypothetical taggant lifecycle in uranium oxide fuels. Introduction of isotopically-perturbed mixtures of elements, at concentrations well above their native background in low-enriched uranium, would allow persistent batch-scale tagging of commercial fuels.

Synthesis of bulk taggant powders from commercially available stable isotope sources is the most straightforward approach to taggant preparation for blending into oxide fuels (Figure 2). Engineered microparticles also have the potential to be an extremely powerful taggant strategy (Williamson, 2019). Because the engineered microparticles encode multiple elemental and isotopic signatures, they have the potential to convey provenance information at the micron scale, with a controlled distribution within a fuel matrix. These particles may survive in reactor environments and provide straightforward fingerprinting of nuclear fuel at a production batch level, before and after use. Unique isotopic mixtures ("double-spikes") may be downblended with the naturally occurring element to extend supplies and reduce cost. The resultant physical feedstocks have targeted isotopic combinations that can be added to fuel forms for irradiation experiments or used as-is for analytical method development and demonstration. More sophisticated taggant design strategies include development of an optimization algorithm to select

ideal mixtures/combinations of potential taggant candidates that meet constraints of front-end verification, back-end nuclear forensics, fuel specifications, and irradiation constraints using convex optimization techniques.

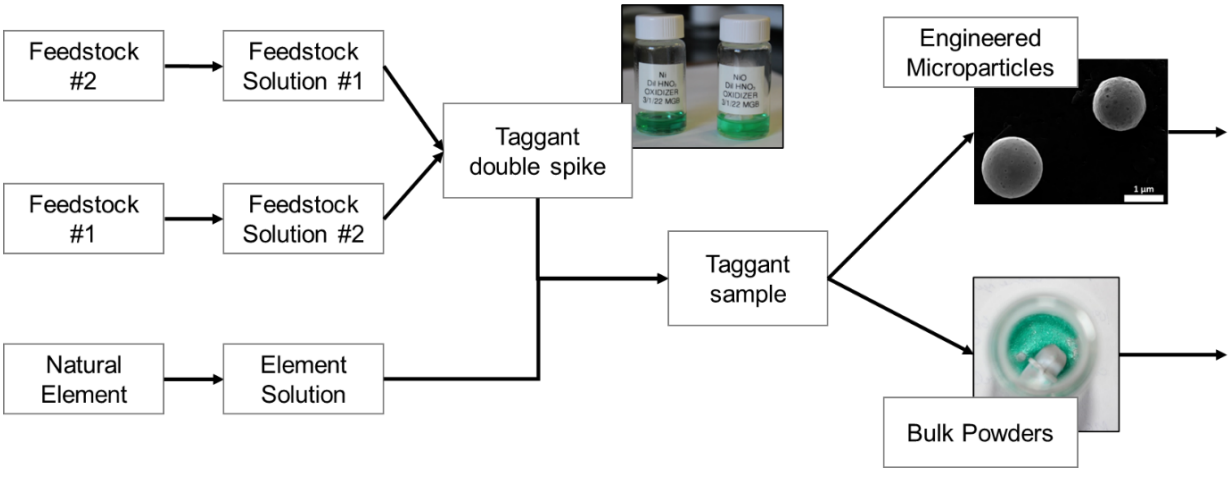

Figure 2. Diagram outlining the preparation of isotopically-barcoded taggant materials with pictures of intermediate solutions of Ni double-spike blends and final solid forms suitable for incorporating into uranium oxide pellets.

To date, the project team has designed and prepared isotopic taggant mixtures enhanced in ^{92,94,97,99}Mo, ^{184,186}W, or ^{61,62}Ni oxides, and incorporated them into sintered uranium oxide pellets at levels between 10-2000 µg/g U. Measurements of the stable isotope ratios of the as-prepared taggants are in progress (Shollenberger, 2023), as well as detailed characterization of the pressed and sintered pellets using SEM-EDS, laser-ablation mass spectrometry, and destructive analysis. A series of irradiation experiments are also in progress using the High-Flux Isotope Reactor at Oak Ridge National Laboratory (Wilson, 2023). Tagged samples will be irradiated for as many as six 23-day cycles, and then removed from the reactor to examine the effect of tagging on their thermomechanical integrity, as compared to untagged pellets (Cheniour, 2023).

In support of predictions of post-irradiation taggant compositions and analyses of cost impacts for reactor operators, a comprehensive analysis of the quality of nuclear data for potential taggants was undertaken. This analysis of the National Nuclear Data Center database included assessment of theoretical and experimental data quality, resonance evaluation, integral metrics, fission product yields, covariances, and accompanying documentation. Evaluation of neutron cross-section data is shown in Figure 3; the x-axis orders the elements by atomic number and the y-axis provides a data quality metric for each stable isotope. Red, black, and green lines correspond to the 1st quartile, the mean, and the 3rd quartile of scoring. This effort resulted in a portfolio of actionable data deficiencies and proposed improvements via experiment, where possible, and supplemented with computational methods, especially machine learning.

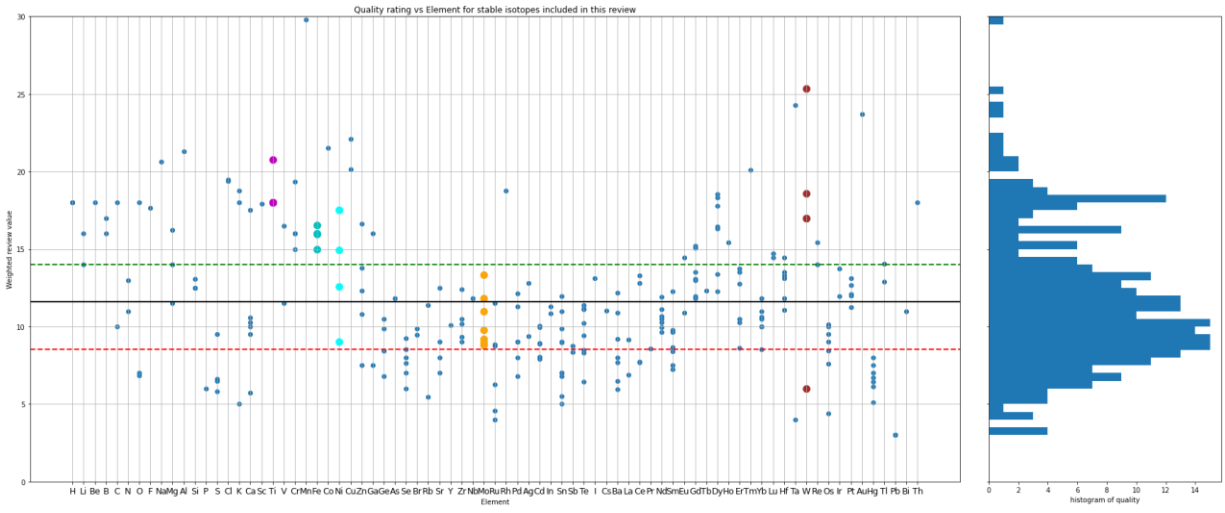

***Figure 3**. Summary of the assessment of neutron capture cross sections for potential taggant elements. Magenta, Teal, Cyan, Orange, and Dark Red circles correspond to isotopes of interest as taggants, namely Ti, Fe, Ni, Mo, and W respectively. The histogram on the right summarizes the population of scores.*

Bulk Taggants for Uranium Metal Fuels: The earliest project initiatives within the Intentional Forensics effort focused on tagging uranium metal fuels, through addition of specific ratios of various elements at their natural isotopic abundances. Metallic fuels of uranium are most often associated with research reactors (U-Mo alloys) and with sodium-cooled fast reactors (U-Zr alloys). Even when diluted through further material processing, the ratios of the taggant elements will, ideally, remain the same. These taggants are detectable through bulk chemical analysis and element-sensitive imaging tools. A secondary tagging strategy also arises since the formation of heterogeneous second phases is likely to occur when alloying elements are added to a metal. To detect these secondary phases, scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) are necessary. Thus, by adding various alloying elements to bulk uranium, two taggant identification strategies are possible: specific ratios of elements and second phase segregation. Initial selection criteria for taggants in uranium metal fuels included melting and boiling temperatures compatible with uranium casting; small to moderate neutron absorption cross-sections; and absence of major health hazards. After initial screening, 16 candidate elements were selected for initial exploratory study of bulk uranium metal tagging: Al, Sc, Ti, V, Mn, Co, Ni, Ge, Nb, Pd, Ce, Tb, Ta, W, Ir, and Au. Those raw elements were combined in sets of four and co-melted in an inert atmosphere of a non-consumable arc melter resulting in four master alloy buttons with four alloying elements per button. Those four buttons were then down blended with depleted uranium to form four baseline alloys, with one button per casting. The plate castings were processed using a vacuum induction melting (VIM) furnace. The plates were then cut up for metallography and machine turnings were taken for chemical analysis. This baseline alloy process is illustrated in Figure 4.

Samples for chemical analysis were taken from two locations per casting, the middle, and the top of the plate. During solidification, alloying elements have the potential to segregate into the last liquid to freeze. The plate castings used in this study mainly solidify from the bottom up, but sampling from both locations confirmed that the elements were equally distributed between middle and top of the plate. Of all the taggant alloying elements, only three (V, Co, and Ir) measured near

their expected values. Most of the taggants were not incorporated into the metal at the desired levels, with noble metals (Pd, Au) and lanthanoids (Sc, Tb) at lowest taggant concentrations in these first castings.. This is likely the result of poor mixing in the master alloy button and/or the VIM furnace casting. In overall order of their incorporation, some chemical groupings become evident: (V, Co, Ni) > Nb > Mn > Ir > Ti > Al > (W, Pd, Au) > (Sc, Tb). Overall, the range of taggant concentrations varied between 100 and 4000 µg/g U.

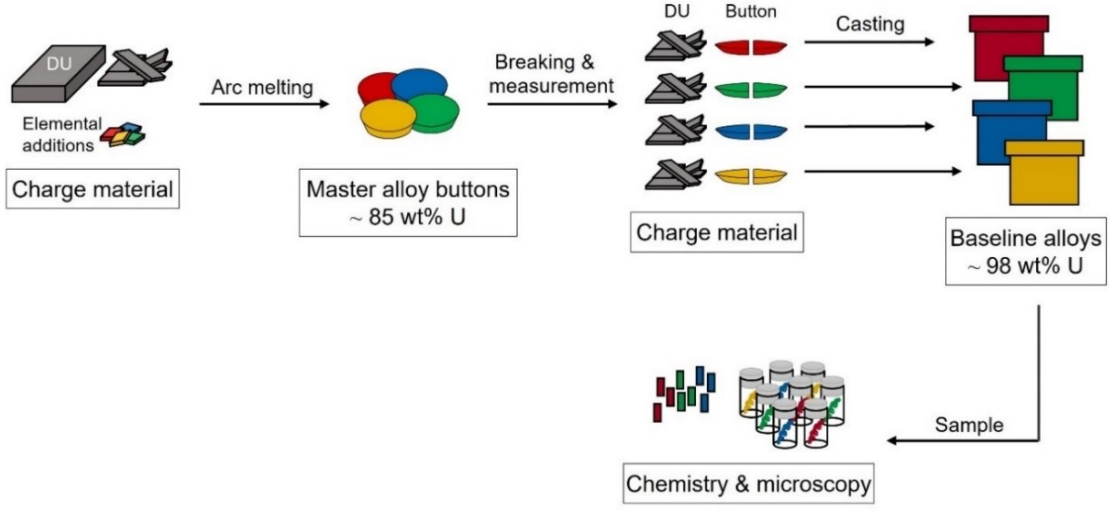

Figure 4. *Schematic detailing the processing of the original baseline uranium alloys.*

Figure 5 provides examples of typical inclusions found within a sample of tagged uranium metal (contains Al, Sc, V and Pd). While constrained by detection limits, SEM-EDS point analysis provides some information on the compositional differences within different parts of this inclusion and the surrounding matrix. In the upper row of images, the angular inclusion in the center consists of Al, Pd, and Sc with no presence of V. In the perimeter directly outside the inclusion, we see combinations of the dopants with the presence of V. Farther away from the inclusion, we detect solely U within the matrix. In another region of the sample (lower images), we observe an angular inclusion and an elongated, rod-like inclusion. Al, Pd, and Sc are present within the angular inclusion, like the first inclusion. However, the rod-like phase contains amounts of V, Al, and Pd with no Sc present. Away from the inclusion, we only detect the presence of U. From a taggant perspective, these inclusions make it easier to locate and identify taggants, but it makes the predictive design of a multi-element taggant difficult since inclusions seem to have different element combinations and concentrations. Additional methods of examining these samples included direct analysis of machine turnings by laser ablation inductively-coupled plasma mass spectrometry. These analyses showed that taggant element mixtures in uranium metal can be readily identified by LA-ICP-MS, with excellent quantitation of intra-element isotopic ratios. Inter-element quantitation proved more difficult, possibly because the contoured surface of the machine turning introduced continuous variations in the focal length of the laser. Alternative methods of sample preparation may mitigate this issue.

The initial suite of elements used in the metal tagging study had striking differences in their propensity to blend with the U alloy, but once incorporated, these taggants did not further partition

through cycles of remelting, blending, and solidification. In aqueous processing studies, dissolution and precipitation partitioned the taggant elements from each other to a significant degree. As for the oxide materials discussed above, taggants containing non-natural stable isotope ratios would overcome this weakness. Future work on uranium metal taggants will progress into studies of taggant incorporation and secondary phase formation in the technologically important nuclear fuels, U-10%Mo and U-10%Zr.

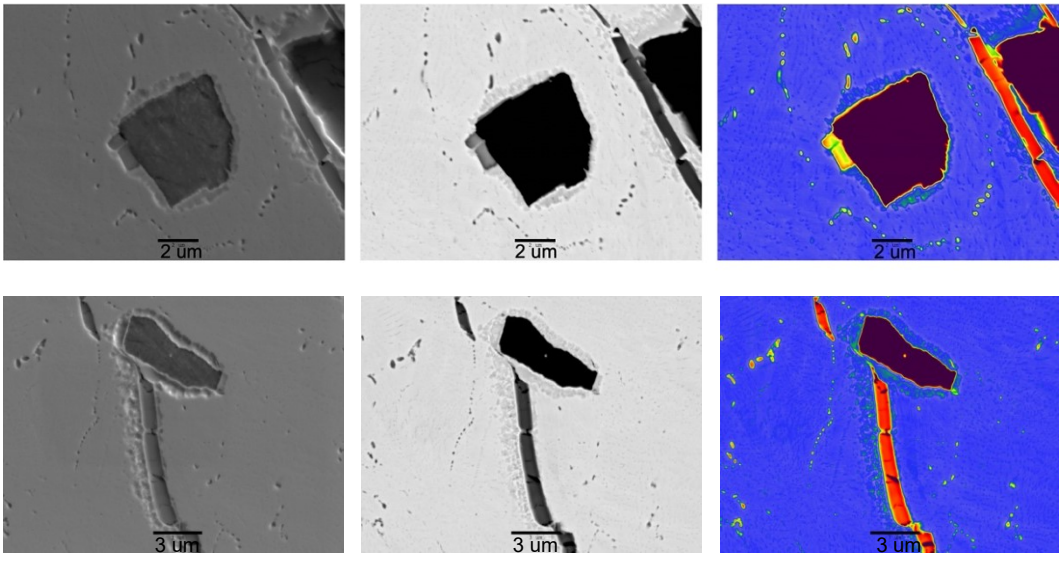

***Figure 5**. Inclusions in U metal tagged with Al, Sc, V, and Pd; observation in secondary electron (left) and backscatter electron (middle) mode. False color images (right) use rainbow lookup table (LUT) to emphasize compositional variation based on mean atomic number (BSE) image.*

Surface Taggants for Fuel Items: Unlike the bulk material tagging processes, which encode a chemical or isotopic signature into the nuclear fuel, surface tagging processes can be used impart a unique identifier onto the surface of a fabricated fuel item, such as a plate or rod. Taggants added to surfaces might also serve as a defense-in-depth strategy to enhance chain of custody procedures for components of a fuel assembly. Surface treatments can be patterned in one or two dimensions (like a barcode or QR code), allowing for rapid identification outside of a laboratory. Application of tags to surfaces is likely to be most beneficial for high-value, low-throughput fuel items.

Initial surface tagging experiments showed favorable results in depositing a secondary metal component onto the base material using a welding heat source (Hackenberg, 2021). Several detectable patterns were produced by placing metal foil over the base material and tracing a pattern with an electron beam over the surface (Figure 6, left). More recently, research was initiated on generating patterned surface tags via atomic layer deposition (ALD), using thin-film interference effects to make the patterning clearly readable under UV observation, while remaining unobtrusive under visible light (Figure 6, center). In addition, a literature review was performed to investigate the use of photoluminescent tags on fuel or clad material, resulting in an investigation of deposition of photoluminescent oxide particles into welds with varying colors and intensities (Figure 6, left).

Durability testing and detection methods for these surface patterning techniques is being investigated along multiple pathways. Laser deposition using metal foils results in tags that are durable to abrasion as a function of the energy of the laser beam imparting different depths of penetration. Detection of laser-deposited tags in the field can be performed using spatially-resolved handheld x-ray fluorescence instrumentation or using point-probe eddy current mapping. Initial durability testing of ALD coatings has focused on their survivability in water and boric acid solutions at elevated temperatures. This work is in its initial stages, but substantial corrosion was observed in ZrO_2 and SnO_2 films, suggesting that corrosion resistance will require different materials. Preliminary EXAFS measurements of the ZrO_2 films at the Advanced Photon Source (APS) indicate some degree of disorder in them. In the future, additional data may be taken at the APS to characterize changes to the films from exposure to corrosive conditions. Other future work will include developing more scalable and repeatable patterning techniques and measuring the effects of heavy-ion irradiation on taggant detectability and substrate integrity, as a precursor to reactor irradiation experiments.

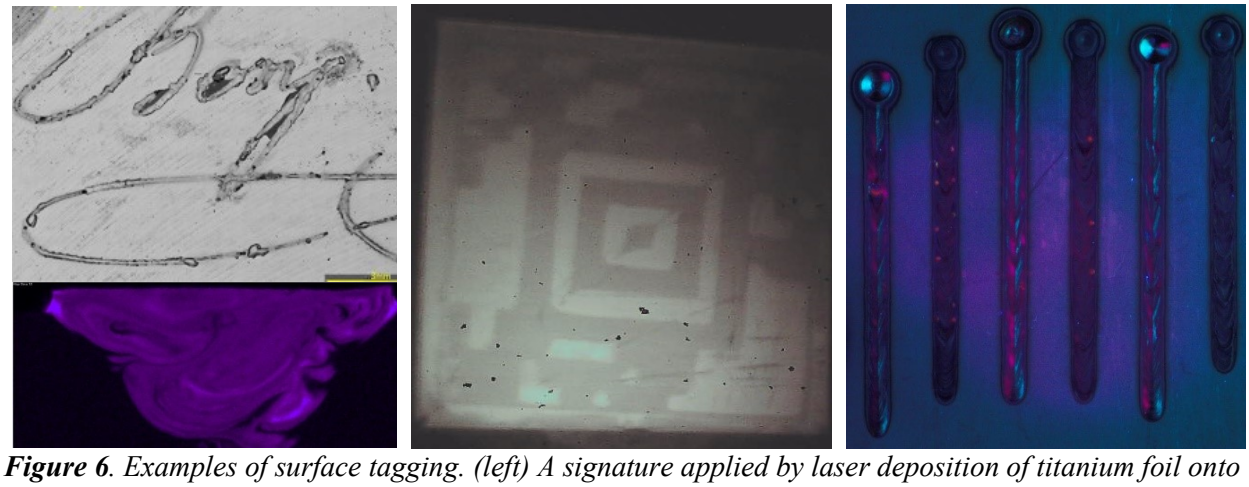

***Figure 6**. Examples of surface tagging. (left) A signature applied by laser deposition of titanium foil onto 304L stainless steel, with its cross-section mapped by SEM-EDS in the lower panel. (center) A 2-dimensional code applied by atomic layer deposition of zirconium oxide (ZrO_2) on an aluminum surface, visualized under UV irradiation. (right) Photoluminescence of europium oxide (Eu_2O_3, left) and aluminum oxide (Al_2O_3) particles embedded in 304L stainless steel by weld deposition.*

Conclusions

The Intentional Forensics Venture, as described in this work, represents a novel and integrated approach to intentional nuclear forensics which seeks to compliment the current nuclear forensics framework though the development of innovative strategies for the tagging of nuclear fuels. This involves the investigation and development of taggant systems which are suitably probative and recoverable during nuclear forensic analysis, durable through various nuclear fuel cycle processes, benign to a nuclear reactor, and cost-effective to implement. To date, the Intentional Forensics Venture has resulted in advancements towards the design, manufacture, and measurement of taggants, including the development of isotopically barcoded, multi-element additives, and surface taggants. Future efforts are expected to include the evaluation of candidate taggants' persistence and safety impacts during irradiation, the development of modeling tools to support taggant design

and evaluation, as well as the exploration of novel candidate taggants and the development of the associated analytical measurement techniques.

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