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Technical note

Age-dating uranium metal using microstructural damage

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ABSTRACT

Current age-dating technologies for uranium metal provide inadequate information when the material is not chemically purified prior to sample formation. The microstructural damage occurring within the lattice of the metal could provide a time-dependent chronometer to enable sample age determination. As isotopes in the metal decay, the recoil particles travel throughout the lattice and dislocate surrounding atoms. Preliminary simulations indicate the feasibility of this method for highly-enriched uranium (HEU) and high assay low-enriched uranium (LEU) while suggesting lower feasibility for enrichments below commercial LEU. These analyses motivate future simulations and experiments to optimize sample preparation for inspection.

1. Introduction

As part of the Nuclear Nonproliferation Treaty, States must declare activities involving nuclear materials—particularly those related to the nuclear fuel cycle. The nuclear fuel cycle encompasses mining, milling, enriching, and fuel fabrication. The fuel may then be dispersed to power or research reactors. Finally, the spent fuel may be reprocessed, recycled, or stored. States must report their activities to the International Atomic Energy Agency (IAEA) in each step of the fuel cycle, with IAEA inspectors corroborating the States' reports and declarations.

Radiochronometric techniques are central to verifying nuclear activities. Radiochronometry utilizes the inherent radioactive properties of nuclear materials to ascertain the time elapsed since material (in its current form) purification. When verifying uranium-based operations, one of the most effective radiochronometric methods involves ^{230}Th and its parent isotope, ^{234}U. Once removed by chemical processes, it takes ^{230}Th approximately 5×10^5 years to reach secular equilibrium, making the U/Th ratio a logical starting point for determining the elapsed time since purification (Harmon et al., 1977; Ikeya and Ohmura, 1983; Mortlock et al., 2005; Lamont and Hall, 2005). However, nuclear materials can be stored in various forms prior to processing, so this method is inapplicable when ^{230}Th is not removed in purification.

While radiochronometric techniques provide exceptional insight into the processing/purification history of certain nuclear materials, recycling nuclear materials can pose significant challenges to traditional radiochronometric techniques. One of the greatest challenges arises in worldwide initiatives to convert highly-enriched uranium (HEU) to low-enriched uranium (LEU) suitable for powering either commercial or research reactors. In this case, uranium (HEU and depleted or natural uranium metal) with disparate purification dates are blended to produce low enrichment metal products without any purification step. Thus, the age-sensitive radioactive decay products necessary for radiochronometric verification techniques are not applicable. When chemical purification is not performed during LEU fuel production, the material will contain a mixture of decay products from the initial feed material, making it impossible to glean any information concerning the processing history of the material. Therefore, it is necessary to develop a method to derive the age of non-chemically purified metallic uranium that is independent of the radiogenic isotopes.

With this in mind, methods must be developed based on the properties that change in the uranium materials over time, but do not directly depend upon the concentration of radiogenic progeny in the material. Geologic and archeological studies have utilized morphological and crystallographic properties to estimate the age of inorganic and metallic specimens. Prior studies have centered on changes in the material properties due to both radiolytic processes and natural diffusion that occur over long time periods. Geologic specimens clearly exhibit radiolytic damage tracks when natural deposits of uranium or thorium are encapsulated within host materials (Seydoux-Guillaume et al., 2009). The

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diffusion and discontinuous precipitation of impurities to grain boundaries has been utilized successfully to estimate the age of archeological silver artifacts (Wanhill, 2003a,b).

When compared to natural uranium and thorium materials, the concentration of radioactive sources (isotopes) is significantly higher in the nuclear fuel materials. Thus, one may observe similar crystallographic and morphological changes in these select materials over much shorter timeframes. While some crystallographic processes may require a long time to become observable, crystallographic damage induced by radiolytic processes can occur over very short periods of time. For example, the damage caused by radioactive isotopes in immobilization host materials has been a significant concern for the short- and long-term storage of actinides recovered from fuel reprocessing (Weber and Matzke, 1986; Weber et al., 1998).

This investigation assesses the applicability of similar methods for determining the time since uranium metal material formation. As a first step in determining the efficacy of microstructural and crystallographic changes, we explore the feasibility of using the microstructural changes due to uranium isotope decay within the uranium metal to date the material.

2. Materials and methods

Solving the aforementioned problem requires first setting several parameters. Applying the age-dating method across a broad spectrum of uranium metal required analyzing several forms of uranium metal with various isotopic contents. Table 1 summarizes the values for relevant materials obtained from the Certified Reference Materials (CRMs) from the New Brunswick Laboratory website.

The model should accurately quantify the damage occurring within the sample specimen by examining the responsible particles and their energies. This required analyzing the decay schemes for U-232, U-234 U-235, U-236, and U-238, with Fig. 1 showing a sample decay scheme for U-234.

Finally, we must set up the simulation method. Because the amount of damage will vary with sample size and the material would eventually be assessed using a Transmission Electron Microscope (TEM), we used the model specimen parameters shown in Fig. 2.

The next step in determining the validity of the proposed age-dating method involved quantifying the damage in the metal. As the recoil particles traverse the metal following decay, they displace other atoms from their positions in the crystal lattice. The cascading atoms form voids within the lattice, deemed "damage sites." Subsequent decays over time create more damage. The radioactive decay process will obey the Bateman equations, which outline a solution for determining the damage (Ehmann and Vane, 1991). We used OrigenARP, which uses a generalized form of the Bateman equations, for our analysis. OrigenARP requires the isotopic concentrations, time scale, and preferred output units as input parameters to determine the number of damage sites over time. It then uses the relevant decay chains for the isotopes to calculate the number of progeny isotopes in g-isotope/g-Uranium Metal (Bowman and Leal, 2000).

Table 1
Isotopic concentrations in weight-% for New Brunswick Laboratory Certified Reference Materials used in the analysis.

CRM	U-234 (w-%)	U-235 (w-%)	U-236 (w-%)	U-238 (w-%)
U002	0.00016	0.01733	<0.00001	99.9825
U005-A	0.0034	0.5	0.00117	99.4955
129-A	0.0052075	0.71183	0.0000096	99.28295
U015	0.00836	1.5132	0.0136	98.462
U045	0.03809	4.4599	0.027483	95.4746
U200	0.1229	19.811	0.2103	79.856
U350	0.2467	34.903	0.1667	64.684
U750	0.588	75.129	0.2502	24.033
U900	0.7735	90.098	0.3337	8.795
U930	1.0759	93.276	0.2034	5.445

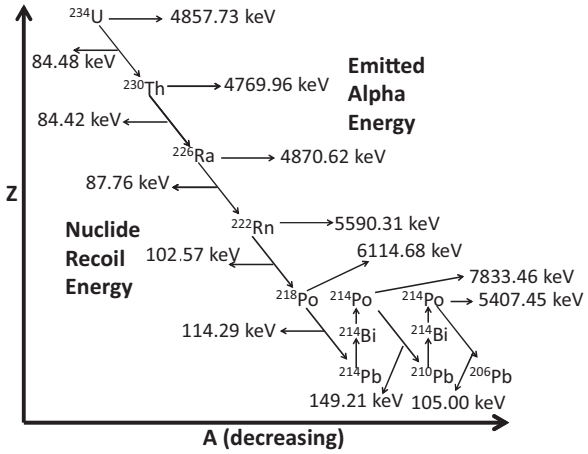

Fig. 1. Decay scheme for U-234 and associated emitted alpha and nuclide recoil energies.

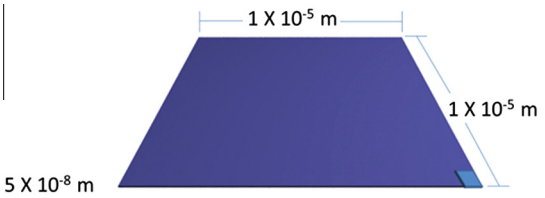

Fig. 2. Ideal TEM specimen, with a volume of 5 μm^3, with a 1 μm^2 portion highlighted.

We can calculate the number of damage sites per unit volume of material from the OrigenARP output in g-isotope/g-U by writing

$$\frac{N_a}{m_u} = \frac{\left(\frac{m_a}{m_u}\right) N_A}{A_a} \tag{1}$$

where m_a is the mass of the isotope, m_u is the mass of uranium metal, N_a is the number of progeny isotope atoms, N_A is Avogadro's number, and A_a is the atomic mass of the progeny isotope.

Since each progeny isotope resulting from an alpha decay creates a damage site, the number of damage sites, D_a, per unit mass of uranium is given by

$$\frac{D_a}{m_u} = \frac{N_a}{m_u} \tag{2}$$

Finally, multiplying the number of damage sites by the density of uranium metal (19.043 g-U/cm^3) and the volume of the model TEM specimen gives the number of damage sites within the model specimen. Fig. 3 shows that the first generation decay of ^{234}U dominates the number of damage sites created in U900.

We next used Transmission Range in Matter (TRIM) (Ziegler et al., 2008) to determine whether TEM can detect the damage sites. TRIM uses the material, material density, recoil particle, recoil particle energy, and the number of ion trajectories as input parameters. We simulated each progeny isotope on every decay chain. We determined the energy for the progeny isotope by multiplying the energy of its corresponding alpha particle by the mass ratio of the alpha particle to the progeny isotope. From these