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Abstract

This is the final report of a three-year, Laboratory Directed Research and Development (LDRD) project at the Los Alamos National Laboratory (LANL). The scientific objective of this project was to develop the ion beam techniques for the characterization of actinides and their effects on other materials. It was designed to enhance our ability to quantitatively understand the oxidation, corrosion, diffusion, stability, and radiation damage of actinides and the materials with which they are in contact. We developed and applied several low-energy nuclear techniques (resonant and nonresonant backscattering, nuclear reaction analysis, and particle-induced x-ray emission) to the quantitative study of the near surfaces of actinide and tritide materials, and determined the absolute accuracy and precision of ion beam measurements on these materials. We also demonstrated the use of variable-energy alpha beams for the study of accelerated aging of polymeric materials in contact with actinide materials.

Background and Research Objectives

The safe long-term storage and disposal of excess special nuclear material with minimal environmental impact is one of the major missions of the Department of Energy (DOE). Past and current storage and processing practices must be modified to accommodate the realities of the end of the Cold War era. This requires a more complete understanding of behavior of special nuclear material (SNM) and the materials with which it is in contact. This project intended to develop and apply ion-beam analytical techniques (Rutherford and resonant backscattering, nuclear reaction analysis, hydrogen detection, channeling, and trace-element particle-induced x-ray emission) to the study of these

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materials and their interactions. This project intended to demonstrate that actinide and tritide materials can be safely measured directly with high accuracy and precision. One of the reasons for using ion beam techniques is to be able to determine the depth distribution of elements without sputtering or removal of material. This nondestructive nature of the measurements minimizes potential contamination problems and simplifies the analysis.

The demonstration of accelerated aging of polymers by ion-beam simulation and analysis of the response of polymers and other materials used in the packaging of SNM, both within a weapon and for external storage, was another objective of this project. The carbon-hydrogen bond strength in polymers is of the order of a few eV, while the alpha particle given off by ^{239}Pu has an energy of approximately 5 MeV, more than enough to cause bond dissociation. Over time, radiolytic action causes the breakdown of the polymer and the generation of gaseous products such as hydrogen, which produces pyrophoric hydride. An additional effect that is important in the context of storage or use of actinides is the interaction of alpha radiation with adsorbed/chemisorbed water vapor. Understanding the undesirable gas generation and pressurization of storage containers is critical to the proper specification of packaging materials and predicting service lifetimes. The damage produced by alpha radiation within a weapons system is also critical to a complete understanding and prediction of polymer lifetimes.

Importance to LANL's Science and Technology Base and National R&D Needs

This project directly addresses the *Nuclear and Advanced Materials* core competency identified by the Laboratory. In particular, it represents a new application and further development of ion-beam materials techniques for microstructural and composition characterization of materials that are key to future missions in nuclear materials processing, use, and storage.

The DOE has identified the maintenance of nuclear weapons technology and competency that is responsive to national security needs as a primary strategic goal. This is directly relevant to the science-based stewardship of nuclear weapons. The Laboratory has a major role in ensuring the successful attainment of this goal through appropriate redirection of competencies developed from the past research, development, and testing mission. DOE Defense Programs has further approved a strategy for meeting the goal of stockpile stewardship. Within this context, this project applies advanced characterization techniques to study the response of nuclear and weapons materials to aging in their unique chemical and radioactive environments.

The downsizing of the weapons complex and the transfer of limited production capabilities to Los Alamos places additional burdens on the advanced analytical capabilities of the Laboratory. To successfully respond to the changing needs of Laboratory, we must upgrade and maintain state-of-the-art analytical facilities and expertise to safely handle these unique materials.

Scientific Approach and Accomplishments

The basic approach was to develop and apply ion-beam analysis techniques to the study of special nuclear material and related materials characterization problems. This ultimately means solving the problem of analyzing a surface with ion beams when the surface itself is a source of alpha radiation. Depending on the level of alpha activity associated with the sample itself, it is sometimes necessary to use backscattering and nuclear reaction analysis with particles other than alphas so that particle identification methods can be used to distinguish the analytical ions from the background. Proton, deuteron, ^3He , or heavy ion backscattering are appropriate alternatives depending on the analytical needs of the particular problem.

Normal, low-energy alpha backscattering is not appropriate for the analysis of light elements such as oxygen and carbon in a heavy matrix such as uranium or plutonium because the scattering cross section, and consequently the sensitivity, is low relative to the scattering from the substrate. It is possible to use the enhanced cross sections of resonant backscattering to measure these light elements quantitatively if the cross sections are known. We therefore prepared standards and measured the resonant scattering cross sections for $^{11}\text{B}(\alpha,\alpha)^{11}\text{B}$, $^{12}\text{C}(\alpha,\alpha)^{12}\text{C}$, $^{14}\text{N}(\alpha,\alpha)^{14}\text{N}$, and $^{16}\text{O}(\alpha,\alpha)^{16}\text{O}$ in the energy range from 2 to 9 MeV. The choice of a particular resonance energy depends on the sensitivity needed and the depth over which the measurement must be made. In general, we found that particularly useful alpha backscattering resonances are at 6.6 MeV for ^{11}B , 7.6 MeV for ^{12}C and ^{16}O , and 8.8 MeV for ^{14}N and ^{16}O .

An example of resonant backscattering is shown in Figure 1, which shows the presence of a thin oxide layer on the surface of a sample of bulk uranium. These types of measurements are very useful for studying oxidation and corrosion of actinides because they are sensitive to changes of a few monolayers of total oxygen at the surface and can be used to measure the subsurface distribution of oxygen with 200-Angstrom depth resolution. Bulk oxygen content is easily measured at the level of 1 - 2 atomic percent relative to uranium. Using a relatively wide resonance to profile the subsurface distribution of light element impurities is preferable to using a very narrow resonance and varying the

incident beam energy. This method was also used to study the oxidation kinetics of TiN, exposed and buried beneath Pt thin films, for the semiconductor industry.¹

Another example of the importance of resonant backscattering analysis for understanding the corrosion behavior of tritiated material was the study of a staining problem associated with the loading of erbium films for neutron tube targets. By combining resonant backscattering and an isotope specific nuclear reaction [$^{18}\text{O}(\text{p},\alpha)^{15}\text{N}$ at 820 keV], we were able to measure and understand the temperature-dependent behavior of oxygen throughout a 5000 Angstrom film of erbium deuteride. Native oxide formation and subsequent oxidation at the outer surface, in the bulk, and at the back interface of a molybdenum substrate were studied *in situ*. It is an example of the complexity of corrosion behavior that can be studied using ion beam techniques.

By their very nature, actinides contain helium and the development of methods to quantitatively study helium effects in these materials is important for the stockpile stewardship program. The ion beam techniques of elastic recoil detection and nuclear reaction analysis provide several flexible approaches to the analysis of materials containing the various isotopes of hydrogen and helium. The usual method for detecting hydrogen in materials involves forward elastic recoil detection of the hydrogen with an incident low-energy alpha beam and the use of an absorber foil. The method has been generalized and extended to the detection of helium in materials by using an incident beam that is heavier and of higher energy. For example, a 20-MeV beam of ^{28}Si has been used to elastically scatter helium out of a AuAg sample. The AuAg samples are surrogates for Pu that have the same stopping power and density. Helium was implanted and subsequently measured using the technique. By performing variable-energy and dose implants, any desired profile concentration can be obtained. The only limitations are those imposed by the straggling of the incident helium ions and the overlapping range distributions. A high dose implant at a single energy will produce a buried layer with bubbles. A series of low concentration implants at variable energies will mimic the more uniform helium concentration profile associated with aging of actinide material.

An example of the use of recoil and nuclear reaction techniques for the analysis of multiple isotopes in materials is the measurement of deuterium, tritium, and protium in erbium thin films used for neutron generator targets. Figure 2 is a spectrum of the elastically scattered deuterium and tritium from a metal film. The incident beam was 12-MeV ^{28}Si and the scattering angle was 30 degrees. Figure 3 shows a combined backscattering and nuclear reaction spectrum obtained from the same erbium film. In this case the incident ion beam was ^3He and the alpha peak is from the positive Q-value nuclear

reaction, $d(^3\text{He}, \alpha)p$. The complete simulation of these spectra enables us to determine the absolute thickness, uniformity, and hydrogen isotope loading ratios of the tritium loaded targets. The absolute accuracy of these measurements is better than 3% and the method has been incorporated into the regular production of components.

In the same way that multiple energy and dose helium-ion implants were used to put helium into a metal surrogate in a desired profile, multiple energy and dose implants were used to produce the same energy-loss distribution in polymeric materials. The relatively constant energy distribution of alpha particles emitted from actinide material has been reproduced by three or more radiations at intermediate energies. The straggling of the alpha beam traversing the material or an absorber foil simulates the degraded energy and angular distribution of surface alpha activity from solid actinide material. This enabled us to accelerate the aging process of polymers due to alpha exposure from actinide material. Accelerated aging irradiations of polymeric materials in contact with actinides in engineered systems have been performed under conditions of temperature, pressure, and residual gas composition corresponding to conditions in the field. The measurement of the radiolytic breakdown products has been demonstrated by mounting a quadrupole mass spectrometer to the scattering chamber at the Ion Beam Materials Laboratory (IBML). Subsequent measurements of the altered mechanical properties of the complex polymeric materials were made.² Follow on programmatic projects involving the engineering divisions from Los Alamos, Oak Ridge, and Livermore Laboratories are continuing.

The potential segregation of alloying elements in actinides during processing, fabrication, or aging is an example of a problem requiring high precision, spatially resolved measurements of composition. Particle induced x-ray emission is an excellent method for obtaining this information, particularly if used in conjunction with alpha backscattering measurements. We installed on the general purpose scattering chamber at the IBML an x-ray detector with multiple filters for making these simultaneous measurements. We have also modified the analysis programs to incorporate x-ray production cross sections for incident ions other than protons. The absolute quantitation depends on not only the x-ray production cross section as a function of energy, but also the energy loss of the incident ion and the absorption of the x-rays as a function of depth. Figure 4 shows an x-ray spectrum obtained from UNb alloy. It is interesting because it used an incident beam of alpha particles and the M x-rays from uranium and the L x-rays from Nb for quantitation. The absolute concentration of the alloying element can be measured to less than 0.1% in a few minutes. Spatial resolution of 0.5 mm^2 is easily obtained in the general purpose chamber and 5 micron resolution is possible with the nuclear microprobe.

We have successfully transported plutonium contaminated samples to the IBML and measured the absolute surface contamination using alpha and heavy ion backscattering. At the extreme lower limits of measurable contamination ($< .001$ of a monolayer), we have found that traditional alpha backscattering is not applicable to realistic substrate materials because of background effects. A non-ideal, but realistic, substrate of stainless steel contains heavy element contamination at the several ppm level and the resulting background limits the ultimate sensitivity of the technique. We have extended the use of heavy ion backscattering using 5-MeV beams of ^{60}Ni to measure the surface contamination of plutonium on real stainless steel substrates at the required lower limits of contamination. We have also installed a time-of-flight spectrometer on another beam line for more detailed experiments involving heavy ion backscattering.

Depending on whether the alpha active material can migrate, measurements can be made in the existing analysis chambers at the IBML or in isolated transfer and analysis chambers with a thin window for beam transport. Except for the case of particle-induced x-ray emission, ion beam analysis involves the measurement of the energies of the particles from a monoenergetic ion beam scattered from the material of interest. The energy loss of the beam in the sample is a measure of the depth distribution of the element being analyzed and any degradation of beam quality results in a loss of depth resolution. The straggling in the energy loss of the beam through a thin isolation window is the limiting factor in the direct analysis of special nuclear material.

Combining alpha backscattering with channeling in single crystal samples enables us to look at the depth distribution of radiation damage in materials. We have extended the method to also measure the depth distribution of damage induced in single crystal material by machining and polishing.^{3,4} Figure 5 shows the experimental setup and typical data obtained from micromachined surfaces. Very detailed information concerning the depth of damage versus depth of cut and direction of the cut relative to the crystallographic direction of the sample were obtained as shown in Figure 6. Finally, by analyzing the energy dependence of the dechanneling, it is also possible to obtain even more detailed information about the nature of the defects produced by machining or polishing. Figure 7 shows presence of deep distortion-type defects in mechanically polished ZnSe.

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Figure 1. Resonant alpha backscattering spectrum taken from a sample of bulk uranium showing the presence of a thin oxide layer containing 35×10^{15} oxygen atoms/cm².

Figure 2. Spectrum of elastically scattered recoil particles from a thin film of erbium deuteride/tritide. An incident beam of 12-MeV ^{28}Si was used to determine the ratio of deuterium to tritium throughout the film.

Figure 3. Combined spectrum of elastically scattered 3He particles from an erbium film and the nuclear reaction products, alphas and protons, from the deuterium in a film of erbium deuteride. Such spectra are used to determine the absolute hydrogen isotope loading in neutron targets.

Figure 4. Spectrum of alpha-excited x-rays from a uranium-niobium alloy used to measure the spatial segregation of the niobium with high precision.

Figure 5. Experimental setup and typical $\langle 0001 \rangle$ channeling spectra obtained from a micro-machined surface of cadmium sulfide: 1) undamaged, chemically etched surface; 2) 10-micron cut along (1120); 3) 10-micron cut along (1010); 4) random unchanneled spectrum.

Figure 6. Maximum depth of damage for $\langle 0001 \rangle$ CdS machined along the (1010) and (1120) directions for various depths of cut. This is typical of the detailed information that can be obtained by careful channeling measurements.

Figure 7. Dechanneling parameter versus depth for a 1/4-micron polished surface of ZnSe showing the presence of distortion-type defects deep below the surface.