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ABSTRACT

The aging in plutonium is predominantly caused by its internal self-irradiation. The self-irradiation in Pu-239 is by the decay process of transmuting the Pu atom into uranium atom and emitting an α-particle. Most of the lattice damage comes from the uranium recoil resulting in Frenkel-type defects consisting of vacancies and self-interstitial atoms, helium in-growth and defect clusters and possibly even though it is not yet observed, the generation of voids. As part of the stockpile stewardship, it is important to understand the changes in the structure and microstructures and their correlations to the physical properties. Changes in the physical properties have a direct relationship to the quality of the structure, in terms of formation of defects and defect clustering, accumulation of voids, grain boundaries, phase changes and etc. which can adversely affect the stability of the material. These changes are very difficult to monitor because of the high activity of the sample, high atomic number making x-ray and synchrotron probe into the bulk very difficult (neutron probe is not feasible) and the long life time which normally requires decades to measure. In this paper we describe the development of an in-situ in-house transmission x-ray diffraction (XRD) experimental technique used to monitor the structural changes in these materials. This technique calls for a very thin sample of less that 2 μm and to accelerate the aging process due to self-irradiation, spiked alloy of 7.5 weight percent of Pu-238 is used. This is equivalent to roughly 17 times the normal rate of aging. Current results suggest that over a period of 2.8 equivalent years, an increase of 0.5% in unit cell parameter is observed. The increase appears to be an abrupt jump at about 1.1 equivalent years, brought about by the collapsing of the atoms from the interstitials to the lattice sites. Further data analysis is on the way.

INTRODUCTION

The aging in plutonium alloy is of great interest to the science-based stockpile stewardship effort [1, 2]. Essentially, the aging process is predominantly caused by its internal self-irradiation of the Pu-239 atoms. Self-irradiation of Pu-239 is by the α-decay process where the atom transmutes into uranium atom of 85 keV and emits an α-particle of 5 MeV. The α-particle then, attracts 2 electrons from the bulk and forms the helium atom. Most of the lattice damage comes from the recoil of the uranium atom resulting in Frenkel-type defects consisting of vacancies and self-interstitial atoms. Significant number of the interstitial atom can also diffuse back into the lattice, a process known as "self-healing" [1, 2]. There can also be defect clustering and possibly even though it is

not yet observed and the generation of voids. As part of the stockpile stewardship, it is important to understand the changes in the structure and microstructures and their correlations to the physical property. As it has been observed and pointed out that, in the nuclear-energy industry reactor steels which are exposed to intense radiation, undergo micro structural changes which includes reduction in density, hardening and embrittlement [3, 4]. Void swelling has also been observed for reactor exposed materials and not for plutonium alloys. These changes are very difficult to monitor because of the high activity of the sample, high atomic number making x-ray and synchrotron probe into the bulk very difficult. Neutron probe is not feasible because of the nuclear reaction with Pu atoms. It is also a problem to monitor the structural changes because of the long reaction time which normally requires decades. It has been pointed out that the radiation damage occurs at a rate of roughly 0.1 dpa (displacement per atom) per year and helium production at roughly 41.1 appm (atomic parts per million) [1]. Previous XRD experiments [5, 6] have observed lattice expansion in 2-3 years. Other physical measurement [4] has indicated that there is a volume change of about 0.15% in 60 equivalent years.

We have designed an in-situ transmission XRD experiment to monitor the structural changes in these materials. In order to monitor the changes in a reasonable time frame, spiked alloy with the more active Pu-238 is used. In this paper, we present our initial XRD results of our measurements for a period of 3 equivalent years for the spiked Plutonium. The peaks positions and profiles are carefully monitored in-situ to determine the changes due to self-irradiation. Unlike previous examination, data acquisition is carried out every 4 hours which is to 2.8 equivalent days. The possibility of phase change can also be monitored. The examination of the evolution of defects, large voids and changes in the microstructures is also underway in this laboratory.

EXPERIMENTAL DETAILS

A very powerful technique in examining the atomistic structural arrangement of any condensed matter is x-ray diffraction. The changes in the lattice parameters can be monitored by the changes in the x-ray peaks positions, the lattice distortion by the peak broadenings and the atomic populations by the peak intensity. The peak shift is expected to be very small and hence, very stable XRD setup is needed.

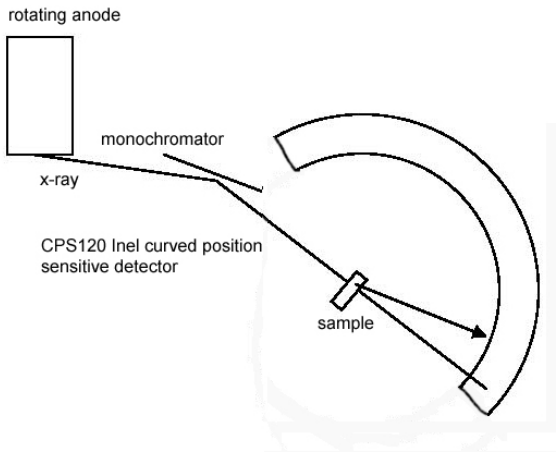

Figure 1: XRD experimental setup

The experiment setup is shown in Figure 1 and it consists of a high intensity rotating anode x-ray source with incident monochromator and a curved CPS 120 detector mounted on a horizontal goniometer. An incident beam monochromator is used. In the experiment described here, copper K_α radiation is used. It is triply encapsulated in the inert atmosphere. In this setup, there are no moving parts during data acquisition thus avoiding any kind of stepping uncertainty. Transmission technique is selected to avoid misalignment due to sample displacement. Also, the advantage of this method is that the probe is on the bulk sample rather than the surface, which can be complicated by the oxide formation. Data acquisition is carried out using the conventional multichannel analyzer fed into a computer. The computer is programmed so that the acquisition is carried out over a period of 60 days at 4 hours interval which is roughly equals to 2.8 equivalent days. Each spectrum is acquired for 2 hours with the x-ray generator setting at constant 35 KeV and 150 mA.

SAMPLE

The sample is prepared to be very small and thin, similar to that used for TEM examination. They are polished and chemically etched. As a consequence of that, there are regions in the sample with thickness of 2 μm or less. Typically for Pu sample, the optimal thickness is only 2 μm for CuK_α radiation and ~12-13 μm for MoK_α radiation [5]. The sample is triply encapsulated in an inert atmosphere using Kapton film. The scattered signals will be greatly reduced for regions greater than 2 μm. The aging decay is accelerated to about 17 times the normal rate by adding a fraction (7.5 wt %) of more active isotope Pu-238 into the Pu-239 lattice.

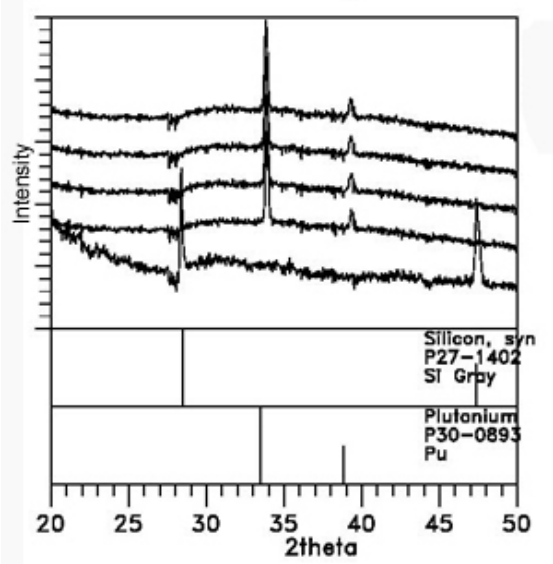

Figure 2: Four XRD spectra for δ-Pu alloy along with a powder Si standard.

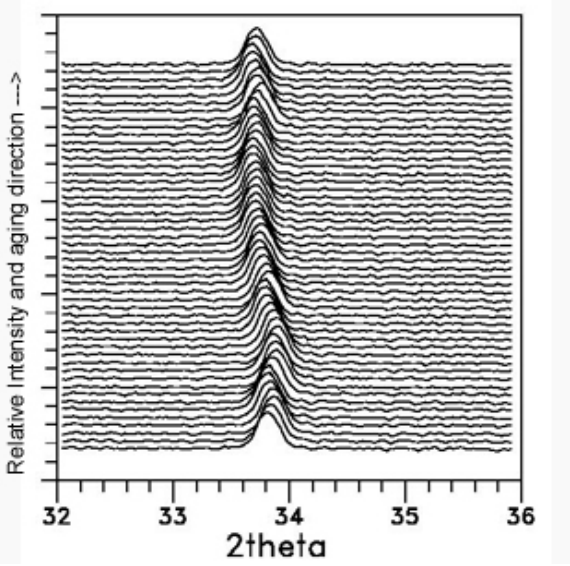

Figure 3: XRD patterns of (111) δ-Pu in the region of 1.1 equivalent years

The sample alloy has ~ 3 atomic percent of gallium. Hence, monitoring the properties of the Pu-238 spiked alloy over a period of 60 days is equivalent to 3 years. At the start of the experiment, the sample is annealed at 300°C for an hour in order to remove any residue defects and lattice strains.

RESULTS AND DISCUSSION

Figure 2 shows typical 4 XRD patterns for δ-Pu, acquired over a period of 16 hours, along with a scan of neat silicon powder as standard. The instrument is calibrated using the silicon peaks, acquired with standard silicon powder loaded onto similar holder at different times. Clearly, the δ-Pu scans show 2 major peaks and they can be indexed to the (111) and (200) lines of the fcc structure. Higher order peaks are not observed due to the high absorption factor of Pu. Using the two δ-Pu peaks and averaging over a number of spectra, the lattice parameter a_o is extracted and found to be 4.584(5) Å at the start of the experiment which is slightly smaller than expected [6, 7].

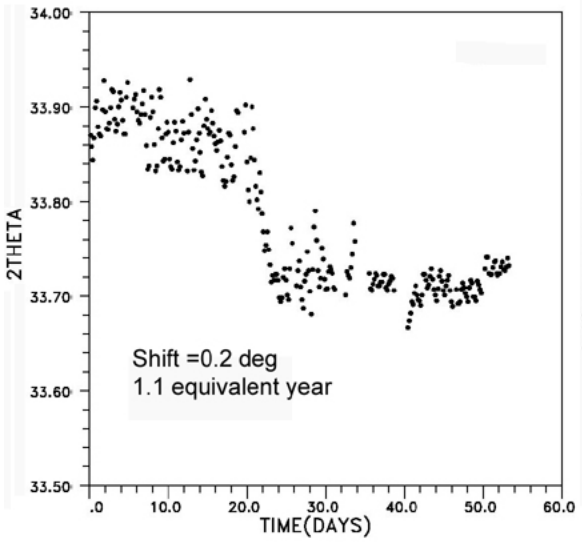

Figure 4: Changes in the (111) peak positions over time

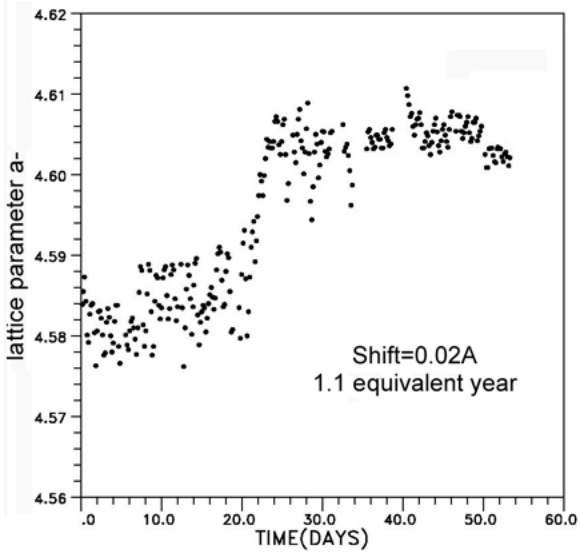

Figure 5: Change of lattice parameter a- over time

Roughly, over 280 spectra are acquired and for simplicity, a few typical plots are shown in Figure 3 in the region of approximately 22 days to indicate the shift in peak position. The lower curves indicate earlier in time and the upper curves indicate later in time. Clearly, a small peak position shift of the (111) reflection to lower 2θ angles can be observed at roughly 22 days of data acquisition which is approximately 1.1 equivalent years. In order to obtain the precise peak position, gaussian curve fitting routine is carried out. The peak positions are then extracted and plotted in Figure 4, indicating that the peak shift is only about 0.2° (2θ) at about 22 days. The peak positions are converted to d-spacing and to the lattice parameter a_o plotted in Figure 5 which shows an abrupt jump in the increase of lattice parameter at roughly 1.1 equivalent years, suggesting an expansion of the unit cell volume. Such behavior has not been observed before. Hence, the experiment was repeated using the same sample and after annealing at 300°C for one hour. Similar behavior is observed. There appears to be a slight increase in the lattice parameter below 1.1 equivalent years, however the error bars are significantly large. The period for this jump is roughly 2.6 days or 44 equivalent days (or 1.5 month) and the magnitude is 0.012 Å which is roughly 0.26% increase in the lattice parameter which is higher than reported for a highly homogenized sample [7]. Further data analysis on the peak intensity and profile is underway in this laboratory.

CONCLUSIONS

These results showed that transmission XRD can be carried out on Pu sample. The setup used consisted of no moving parts during data acquisition hence, accurate peak positions could be carefully monitored throughout the whole period. CuK_α radiation is used which allows for the expansion of the peak profile as compare to the more penetrating MoK_α which collapses the peak width. The above results indicate that the lattice defects in

terms of, most probably lattice vacancies, as the result of self-irradiation of the Pu atoms could be detected and reasonably monitored over a period of 3 equivalent years using a spiked alloy. The change is observed by the expansion of the lattice parameter of about 0.26 % at about 1.1 equivalent years. Further data analysis and interpretations are underway in this laboratory.

ACKNOWLEDGMENTS

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