

EXPERIMENTAL DETERMINATION OF METAL FUEL POINT DEFECT PARAMETERS

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Nuclear metallic fuels are one of many options for advanced nuclear fuel cycles because they provide dimensional stability, mechanical integrity, thermal efficiency, and irradiation resistance while the associated pyro-processing is technically relevant to concerns about proliferation and diversion of special nuclear materials. In this presentation we will discuss recent success that we have had in studying isochronal annealing of damage cascades in Pu and Pu(Ga) arising from the self-decay of Pu as well as the annealing characteristics of non-interacting point defect populations produced by ion accelerator irradiation. Comparisons of the annealing properties of these two populations of defects arising from very different source terms are enlightening and point to complex defect and mass transport properties in the plutonium specimens which we are only now starting to understand as a result of many follow-on studies. More importantly however, the success of these measurements points the way to obtaining important mass transport parameters for comparison with theoretical predictions or to use directly in existing and future materials modelling of radiation effects in nuclear metallic fuels. The way forward on such measurements and the requisite theory and modelling will be discussed.

We bring to the attention of the reader that this article is based wholly or in part on earlier publications of the authors.

1. BACKGROUND

The physical metallurgy of δ -phase plutonium, particularly those aspects related to radiation damage and associated vacancy and self-interstitial properties, is technologically important, and yet still requires a deeper fundamental understanding. Low-temperature damage-accumulation, and subsequent isochronal-annealing provide an experimental methodology for determining important mass transport parameters based on chemical rate equations, e.g., the interstitial migration energy and the vacancy migration energy [1]. The starting point for deducing these parameters is the ability to perform high fidelity annealing experiments. Although annealing experiments have been reported for δ -stabilized Pu(Al) [2,3], the fidelity of the data was limited, and hence the analyses were only qualitative. Previously we reported high-fidelity isochronal-annealing curves of the damage induced electrical resistance for self- and proton-irradiated Pu(Ga) [4]. The annealing properties were measured on a δ -stabilized alloy, Pu(3.3 at.%Ga), an *fcc* δ -phase of plutonium which was resistant to the martensitic phase transformation to the α' -

phase at all temperatures of these experiments. An important element of the earlier work was the experimental determination of the temperature for the various annealing Stages I to V.

2. DAMAGE ACCUMULATION AND ANNEALING IN δ -PHASE Pu(Ga)

We measured, as near to the dilute limit as was practical, the temperature dependence of the resistance of radiation damage in the form of defect ensembles produced by low-temperature damage-accumulation and subsequent annealing [4]. Fig 1 shows the isochronal data for self-irradiation damage accumulation and for proton irradiation. We note, that while the proton irradiation appears to be typical of an annealing curve for a dirty alloy, with no clear indication of interstitial annealing stages, the self-irradiation annealing curve is strongly structured showing a modified Stage I, a Stage II and vacancy Stages III to V. It is interesting to compare the annealing curves with empirical estimates for other metals given by Ehrhart [5] that are shown in Table. The largest difference between experiment and empirical estimates is for Stage V, the temperature where vacancy

clusters become unstable. It is also noteworthy that with respect to vacancies, Stages III to V are indistinguishable as to the origin of the damage, self-irradiation or protons. We note that the long Stage II for the self irradiation is likely associated with a wide range of vacancy impurity interactions as vacancy clusters formed during the cascade relaxation dissolve and migrate through the system. In the case of the proton irradiation all we can say at this time is that Stage I and Stage II are inexorably

combined and that the structureless nature of the monotonic decrease here is likely indicative of the same complex interstitial impurity interactions. Within the resolution of both annealing curves in Fig. 1 we can also note that Stage IV is identical indicating that at this point in the annealing process the remaining vacancy populations are indistinguishable as to their origin, cascade or isolated pairs.

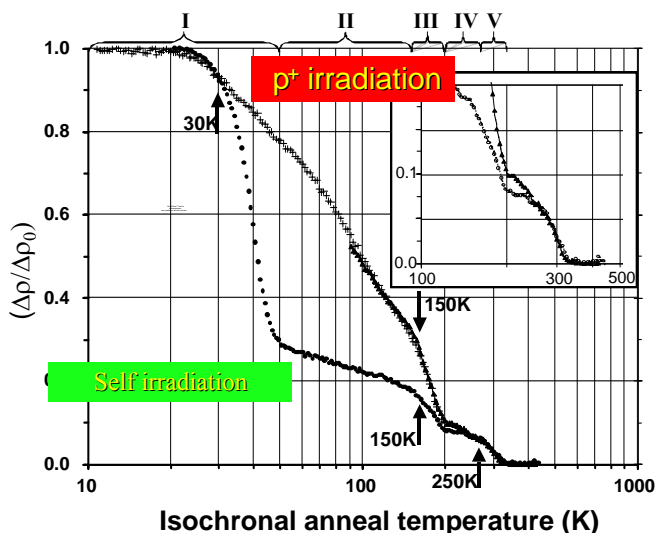


Fig. 1. Isochronal annealing curves for Pu(3.3 at% Ga) irradiated with self-decay and with protons. The isochronal time was 300 s

Empirical estimates for Stage I, Stage III, and Stage V transitions as a function of the melting temperature T_m [5]

	T_m (K)	T_I (K) measured	T_{III} (K) (0.02 ± 0.015) T_m predicted	T_{III} (K) measured	T_{III} (K) (0.2 ± 0.02) T_m predicted	T_V (K) measured	T_V (K) (0.45 ± 0.03) T_m predicted
Pb	601	4	12±9	160	120±12	290	270±18
Al	933	37	19±14	220	187±19	----	420±28
Pu(Ga) 3.8MeV p ⁺	953	~35	19±14	180±5	191±19	310±5	429±29
Pu(Ga) α-decay	953	45±5	19±14	180±5	191±19	310±5	429±29
Ag	1235	28	25±20	230	247±25	540	556±37
Au	1337	----	27±20	290	267±27	530	602±40
Cu	1356	38	27±20	250	271±27	605	610±41
Ni	1726	56	35±26	340	345±35	750	777±52

The annealing data for Pu(3.3 at.%Ga) with a 300 s isochronal anneal is shown in Fig. 1. Stage I for the p⁺irradiation of the Pu(Ga) is not clear but appears to be ~35 K. For the other Stages statistical errors are indicated. Longer anneal times will shift the transitions to lower temperatures, but no more than ~10 K.

Effective activation energies can be deduced from annealing data by varying the rate, α , or time interval for the annealing while determining the transition temperature, T . Fig. 2 illustrates the result of such an experiment for Pu(Ga) showing the shift in the

annealing curve to higher T with shorter annealing time. Here the damage accumulation time was 5 days and the two isochronal anneal times were 100 s (blue points) and 300 s (pink points). The formula for extracting the activation energy, E , is:

$$\ln\left(\frac{\alpha_2 T_1^2}{\alpha_1 T_2^2}\right) = \frac{E}{k} \left(\frac{1}{T_1} - \frac{1}{T_2} \right). \quad (1)$$

The following activation values were deduced: Stage I: 0.05 to 0.1 eV, Stage III: 0.5 eV, and Stage V: 1.0 to 1.3 eV.

During this study we discovered that the specific resistivity for vacancies and vacancy clusters was exponentially temperature dependent. Fig. 3 shows the relevant data. Here we show the temperature dependence of the resistance for three vacancy defect

populations that were produced via damage accumulation at 10 K for 5 days followed by annealing at 30, 150 and 250 K. This result is a spectacular violation of Matthiessen's rule [6,7] for vacancy-defects in δ -stabilized Pu(3.3 at.%Ga) and suggests a Kondo-like impurity behaviour for vacancies in this system. This observation motivated magnetization studies of self-damaged Pu and Pu-alloys.

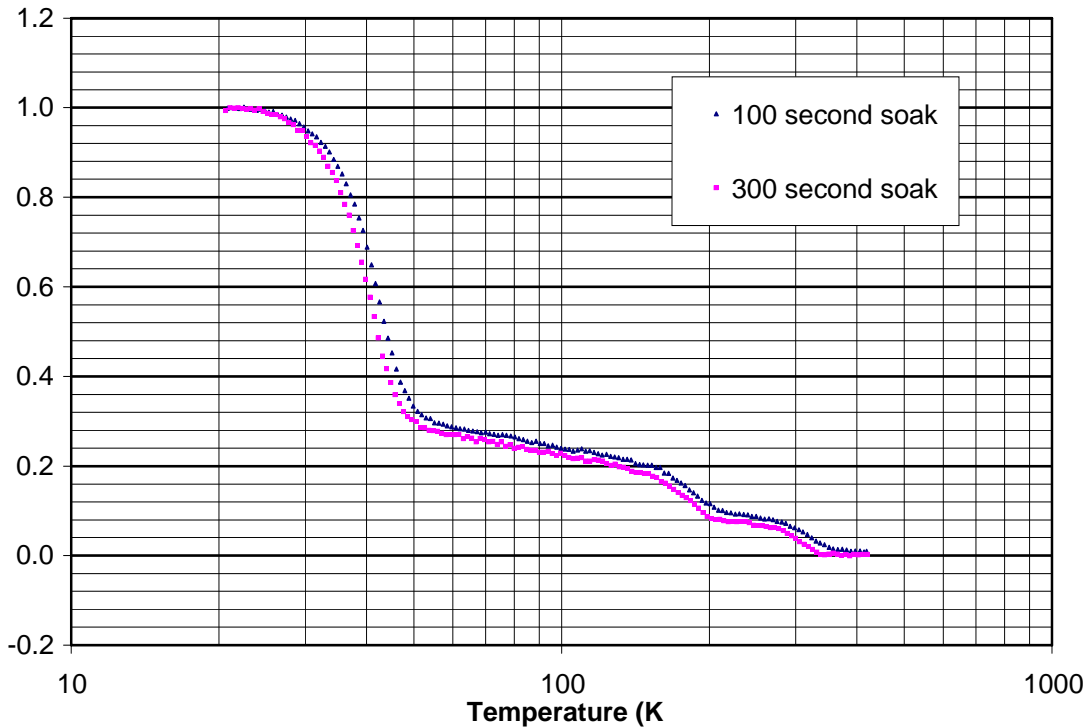


Fig. 2. Two isochronal annealing curves, 100 and 300 s annealing times for each point used to deduce activation energies

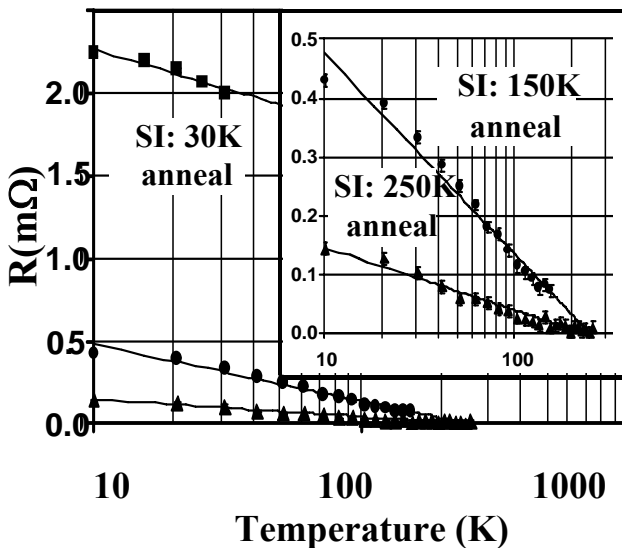


Fig. 3. The resistance for the three defect-populations resulting from self-irradiation (labeled SI) of Pu(Ga) at $T=10$ K for 5d and then annealed successively at $T_i=(30$ K(ν), 150 K(λ), and 250 K(σ)) for 1h prior to measuring the plotted resistance data at a set of temperatures, T_j . The $T(K)$ axis refers to the T_j values of the data points. The inset shows the same data for the self-irradiations at 150 and 250 K where the common $\ln(T)$ axis intercept is evident and the systematic deviation of the data points at 10 K is seen

3. EMERGENCE OF MAGNETISM DUE TO DISORDER

Despite the importance of the $5f$ electrons in defining structure and physical properties of Pu, there is no experimental evidence that these electrons localize to form magnetic moments in pure Pu. Instead, a large temperature-independent Pauli susceptibility indicates that they form narrow conduction bands. We have shown previously that radiation damage from the alpha-particle decay of Pu creates numerous defects in the crystal structure, which produce a significant temperature-dependent magnetic susceptibility, $\chi(T)$, in both α -Pu and δ -Pu (stabilized by 4.3 at.% Ga) [8]. This effect is

reversible by thermal annealing above room temperature. The magnetic and resistive annealing curves for the α - and δ -Pu are shown in Fig. 4. The reader should note that while the annealing curves for resistive and magnetically tracked annealing in α -Pu are quite similar, the corresponding curves for Ga stabilized δ -Pu are quite different with regards to the first annealing stage, the stage associated with interstitial mobility. This suggests that while in the monoclinic α -Pu both interstitials and vacancies contribute to the magnetization, in the more open *fcc* δ -Pu lattice vacancies dominate.

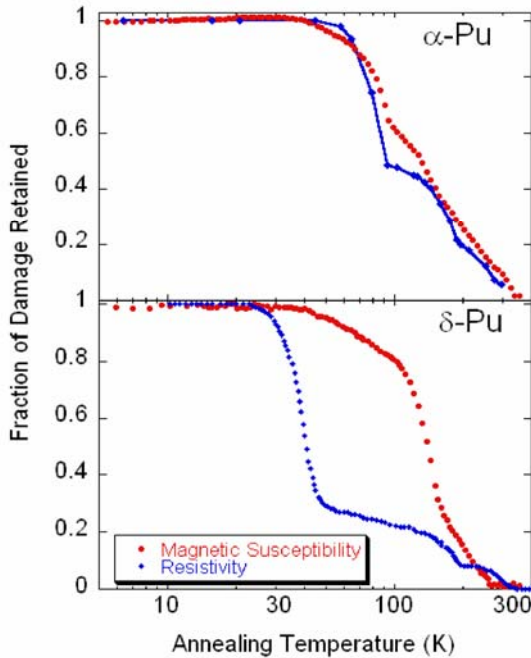


Fig. 4. Isochronal annealing curves for α -Pu and Ga stabilized δ -Pu illustrating that damage is frozen in place below ~ 30 K. The red circles are the magnetic susceptibility measurements from reference [8] while the blue diamonds are resistivity data taken from references [3] and respectively [4]

Fig. 4 illustrates that below 35 K, the radiation damage is “frozen” in place, permitting the evolution in time and temperature ($T < 35$ K) to be studied systematically. By accumulating damage over a sufficiently long time while measuring the susceptibility, χ as a function of temperature,

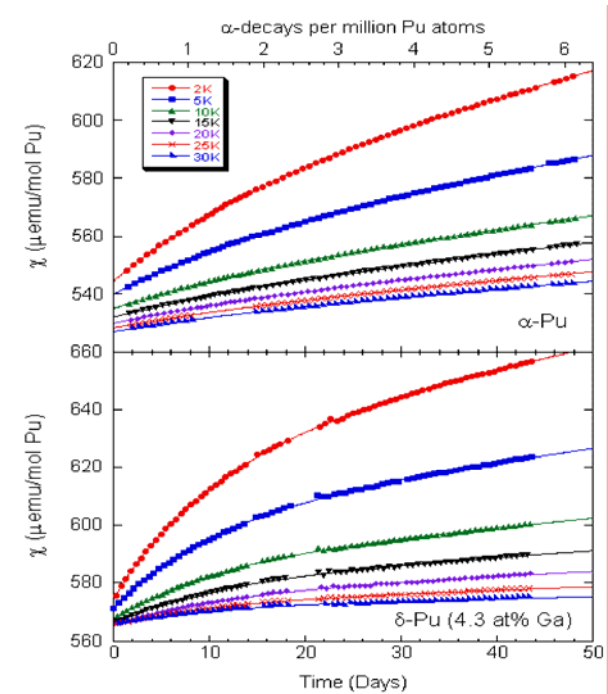


Fig. 5. Representative isothermal magnetic susceptibilities for α -Pu and δ -Pu (4.3 at.%Ga) plotted as a function of time (proportional to the number of α -decays). The lines are fits to Eq. (1) described in the text

T, we could produce susceptibility isotherms for the α -Pu and for the δ -Pu. These isotherms are described by a single formula with one materials dependent variable, the time constant τ .

$$\chi(t, T) = \chi_i(T) + \chi_v(T)(1 - e^{-t/\tau}) + \chi'_D(T)t. \quad (2)$$

Here, $\chi_i(T)$ is the magnetization of the undamaged sample, while $\chi_v(T)$ and $\chi_D(T)$ arise from self damage. The temperature dependence of $\chi_v(T)$ obeys the Curie-Weiss law from which we deduce that self-damage creates localized magnetic moments in previously nonmagnetic plutonium. While Eq. 2 may not be a unique description of the data in Fig. 5 it allows us to extract the dimensional nature of the disorder induced magnetism. In the context of Eq. 2, the parameter τ is proportional to an arbitrary volume around the damage produced by the U recoil and the alpha particle, which, because of disorder, exhibits an effective magnetization. We determined, by fitting the experimental data to Eq. 2, that this volume includes many more atoms (500,000) than are displaced by the damage cascade (3000) estimated from molecular dynamics.

4. LATTICE EXPANSION WITH AM

Plutonium and its simple binary alloys are known to be extremely sensitive to impurities, defects, and as we have shown above, particularly disorder. In earlier work we have added disorder by alloying plutonium with americium, $\text{Pu}_{1-x}\text{Am}_x$, forming a stable fcc phase (δ -Pu, β -Am) from $0.06 < x < 0.80$ where the lattice parameter increases with x [9]. The electronic structure of americium is $5f^6$, thus it has a $J=0$ ground state and its magnetic susceptibility is primarily due to a large Van Vleck contribution [10]. Being a single ion effect this should be independent of the local environment and thus should be insensitive to radiation damage. Therefore, any changes observed in the magnetic susceptibility of the PuAm alloys that deviate from a simple linear combination of the two end members should reflect a change in the magnetic properties of the plutonium. Preliminary results indicate that the expanding of the lattice as a function of Am concentration (negative pressure) results in a tendency of the temperature dependent partial susceptibility for the Pu sub-lattice to exhibit a functional form which is indicative of spin fluctuations. Additional disorder is added to the alloys through the radioactive decay of Pu and Am each of which produces a ~ 5 MeV α -particle and a corresponding recoil (U or Np) that creates a large number of vacancies

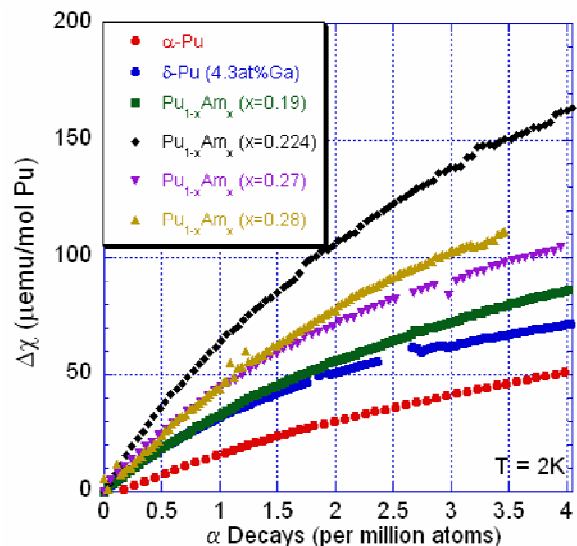


Fig. 6. Increase in magnetic susceptibility per mol Pu due to self damage accumulated at low temperatures. Apart from the 22.4% Am specimen, the effect increases with increasing lattice constant. The curvature as a function of damage suggests this effect is saturating

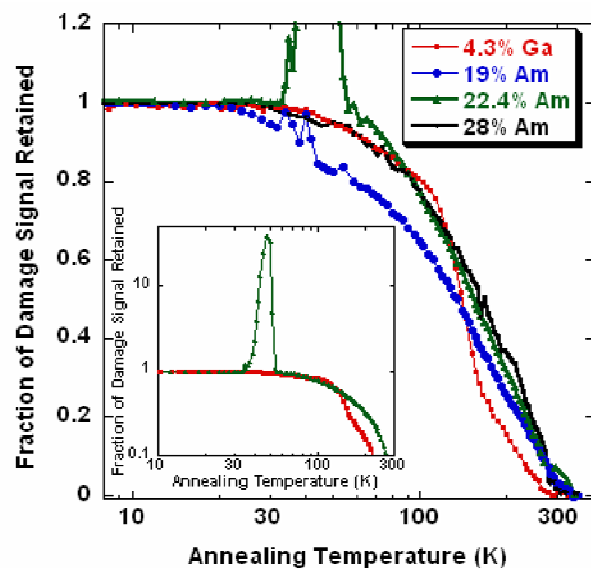


Fig. 7. Isochronal annealing curves for delta phase Pu specimens. The distinct features of the 4.3 at.% Ga stabilized phase are smeared out in the $\text{Pu}_{1-x}\text{Am}_x$ alloys. The 22.4% Am alloy shows a remarkable increase in magnetization near Stage I, that is more clearly illustrated on a log scale in the inset. Similar but less dramatic features are observed in the 19% Am alloy. This “reverse annealing” may be indicative of a damage induced metastable phase

and interstitials, of which a substantial fraction, after relaxation, remain frozen in place at low temperatures. Disorder from self-damage increases with time and is observable through magnetic susceptibility measurements, where Curie Weiss behavior evolves and thus demonstrates the creation of local magnetic moments. These emergent moments may be removed by thermal annealing, proving they arise from the disorder created by vacancies and interstitials. Radiation damage studies on $\text{Pu}_{1-x}\text{Am}_x$ alloys thus allow investigation of how inherent chemical disorder and structural disorder each influence the behavior of the electronic structure of plutonium. In Fig. 6 we observe accumulating magnetization for a suite of Pu(Am) alloys as well as for Pu and Pu(Ga). The data are plotted against alpha decays per (Pu+Am) atoms. While there is a trending in the data, what stands out is the much larger response of the 22.4% Am alloy. Careful annealing studies reveal a new low temperature phase here to fore unknown.

In alloys, as opposed to intermetallic compounds, the distinct phases of annealing may be smeared out due to the disorder inherent in the system. This is shown in Fig. 4 where the distinct stages observed in the Ga-stabilized δ -Pu are no longer readily extracted from the PuAm alloy curves. A second feature, abundantly clear in the 22.4% Am specimen is an anomalous increase in the signal retained with increasing temperature, where the signal grows to $\sim 40X$ the initial damage signal near the temperature where Stage I annealing takes place in other alloys. This is illustrated in the inset of Fig. 7, where the “fraction of damage signal retained is shown on a log-log plot along with the Ga-stabilized Pu specimen. The 19% Am curve shows a similar tendency beginning at roughly the same temperature, although it is much less dramatic. In the simple picture of annealing out damage, the curve should monotonically decrease for each higher temperature since less damage is retained after successive anneals. Small increases in annealing curves have been observed previously [11] for several other alloys such as Cu_3Au , where the increase in signal was termed “reverse annealing”. One explanation for such behaviour is that the radiation damage is either disordering an

ordered intermetallic system, or creating small ordered regions in an otherwise disordered system.

5. CONCLUSION

We have outlined defect accumulation and annealing experiments conducted on Pu, Pu(Ga) and Pu(Am) over several years. Our purpose is to illustrate to the reader that many important defect properties of Pu and Pu alloys are experimentally accessible. However, and even more importantly we wish to caution that there are complexities associated with the solid-state physics of Pu and to a larger extent the 5f series, and these complexities can and do affect the defect properties. The energy differences for the various solid-state phases of Pu are of the order of mRyd. Hence the entropic consequences of this order dependent magnetism are likely to play an important role in Pu and Pu alloys affecting the energy surfaces of various properties such as mass transport, phase transformation kinetics, and phase stability.

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ЭКСПЕРИМЕНТАЛЬНОЕ ОПРЕДЕЛЕНИЕ ПАРАМЕТРОВ ТОЧЕЧНЫХ ДЕФЕКТОВ В МЕТАЛЛИЧЕСКОМ ТОПЛИВЕ

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Ядерное металлическое топливо является одним из многих вариантов прогрессивного ядерного топливного цикла, поскольку оно обеспечивает размерную стабильность, механическую целостность, тепловой коэффициент полезного действия и радиационную стойкость, в то время, как пиротехнология технически относится к проблемам распространения специальных ядерных материалов и их перенацеливания. В данном сообщении мы обсудим последние успехи, достигнутые нами при изучении изохронного отжига каскадов повреждений в Pu и Pu(Ga), которые возникают в результате самораспада Pu, а также характеристики отжига невзаимодействующих точечных дефектов, образованных при облучении в ускорителе ионов. Сравнения этих двух популяций дефектов, возникающих при разных исходных условиях, проливают свет и указывают на сложные свойства дефектов и массопередачи в образцах плутония, которые мы только сейчас начинаем понимать в результате многих модифицированных исследований. Однако, что более важно, успех этих измерений указывает на путь получения важных параметров массопереноса для сравнения с теоретическими предсказаниями или для непосредственного использования при моделировании радиационных эффектов в уже существующих и будущих материалах в качестве ядерного металлического топлива.

Мы обращаем внимание читателя на то, что эта статья основана целиком или частично на более ранних публикациях авторов.

ЕКСПЕРИМЕНТАЛЬНЕ ВИЗНАЧЕННЯ ПАРАМЕТРІВ ТОЧКОВИХ ДЕФЕКТІВ В МЕТАЛЕВОМУ ПАЛИВІ

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Ядерне металеве паливо є одним із багатьох варіантів прогресивного ядерного паливного циклу, оскільки воно забезпечує розмірну стабільність, механічну цілісність, тепловий коефіцієнт корисної дії і радіаційну стійкість, в той час, як пиротехнологія технічно відноситься до проблем про розповсюдження спеціальних ядерних матеріалів та їх перенасичення. У даному повідомленні ми обговоримо останні успіхи, досягнуті нами при вивченні ізохронного відпалу каскадів пошкоджень в Pu і Pu(Ga), які виникають в результаті саморозпаду Pu, а також характеристики відпалу невзаємодіючих точкових дефектів, які утворились при опроміненні у прискорювачі іонів. Порівняння цих двох популяцій дефектів, виникаючих при різних вихідних умовах, проливають світло та вказують на складні властивості дефектів і масопередачі в зразках плутонію, які ми починаємо розуміти тільки зараз у результаті багатьох модифікованих досліджень, Однак, і це більш важливе, успіх цих вимірювань вказує шлях отримання важливих параметрів масо переносу для порівняння з теоретичними прогнозуваннями, або для безпосереднього використання при моделюванні радіаційних ефектів у вже існуючих та майбутніх матеріалах у якості ядерного металевого палива.

Ми звертаємо увагу читача на те, що ця стаття заснована повністю або частково на більш ранніх публікаціях авторів.