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Effect of radiation on bulk swelling of plutonium alloys

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Abstract

Several studies show that plutonium alloys present bulk swelling. More precisely, length (as measured by dilatometry) and lattice parameter (as measured by X-ray diffraction) increase with time and seems to reach saturation after a few months for the microscopic scale. This bulk swelling can be correlated to self-induced radiation due to the decay of the different plutonium isotopes (^{238}Pu, ^{239}Pu, ^{241}Pu and ^{242}Pu) which also induce helium that tends to forms clusters, then bubbles. Many experimental and theoretical results have already been published on this topic. The goal of this paper is to review some of the results and to propose a strategy for both experiments and modelling to try to answer some of the remaining questions regarding swelling and more generally self-irradiation defects in plutonium alloys.

1. Introduction

Among the actinides, plutonium is certainly the most complex element due to its intermediate position in the series. It is usually used when stabilized at room temperature in the face cubic centered δ-phase by adding elements such as aluminium, americium, cerium or gallium.

Plutonium is a radioactive element, and it is self-irradiated due to the decay of the different isotopes, which leads to the creation of displacement cascades from which vacancies, interstitials and clusters remain after thermalization.

After a presentation of the plutonium alloys, a review of the phenomena induced by irradiation and helium will be briefly presented. We will then describe characterizations that have been made on samples: classical high temperature dilatometry, optical fibre dilatometry and X-ray diffraction.

2. Plutonium alloys

Pure plutonium undergoes several phase transformation from the α monoclinic phase at room temperature up to the ε-phase before liquidus at 639 °C. These transformations induce a volume change around 20% as can be seen in Fig. 1 [1]. Moreover, pure plutonium has poor mechanical properties: it is brittle at room temperature.

So in order to avoid all these drawbacks, plutonium is alloyed in order to stabilize the δ-phase at room temperature. This is obtained by adding so-called deltagen elements such as aluminium, americium, cerium or gallium. Fig. 1 shows some dilatometry results for pure plutonium and plutonium alloyed with 3 and 4.5 at.% of gallium [1]. This way it is possible to stabilize the δ-phase from room temperature up to around 500 °C.

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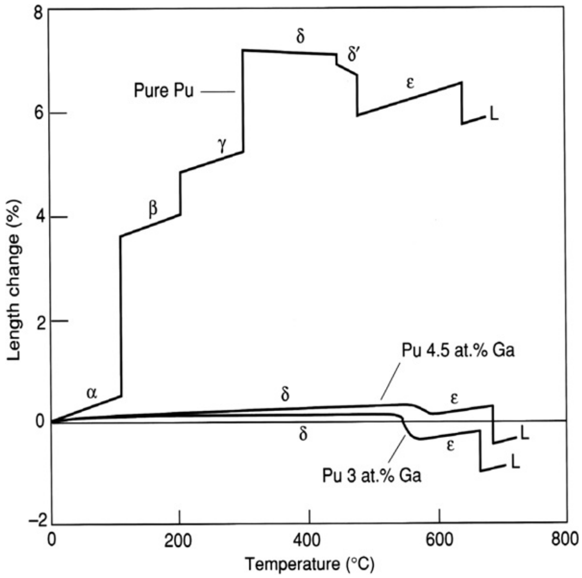

Fig. 1. Expansion of plutonium alloys versus temperature.

The plutonium–gallium phase diagram determined by ELLINGER is given in Fig. 2 [2]. It has been demonstrated that this diagram is the metastable diagram. The equilibrium phase diagram has been given by Chebotarev, leading in particular to the formation of $\alpha + Pu_3Ga$ at room temperature under long time pressurization loading [4] (Fig. 3). As a result, the Pu–Ga δ-phase is metastable at room temperature. So one of the evolutions that could be induced by irradiation could be the destabilization of the δ-phase around room temperature.

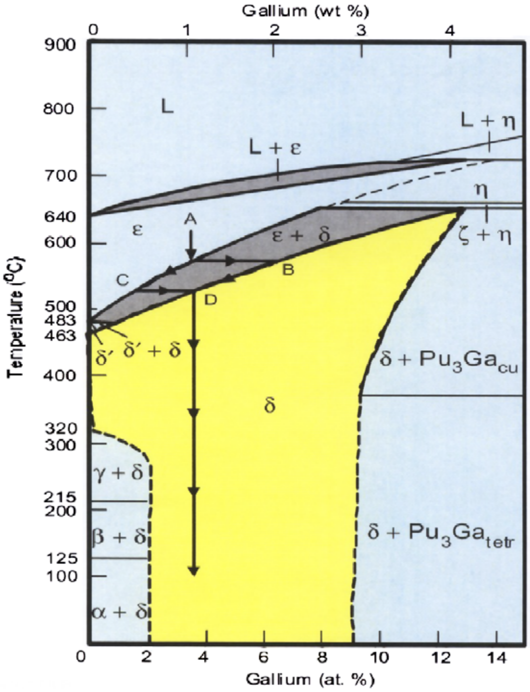

Fig. 2. Ellinger phase diagram of plutonium–gallium alloys.

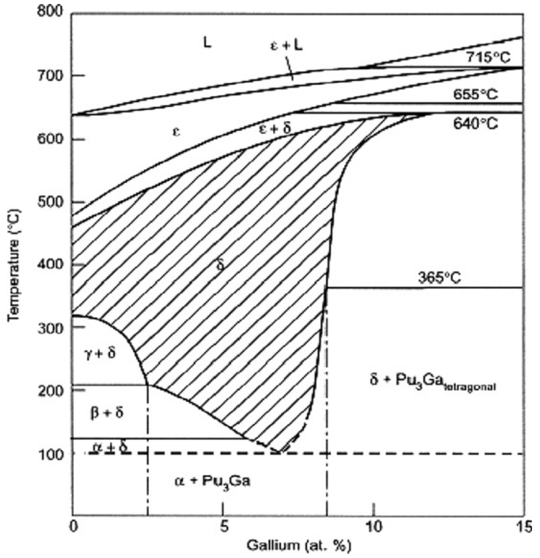

Fig. 3. Chebotarev phase diagram of plutonium–gallium alloys.

Aging of plutonium is given in Fig. 4 and can be described by the following equations:

- ${}^{238}Pu \rightarrow {}^{234}U + {}^{4}He \quad \lambda = 86$ years
- ${}^{239}Pu \rightarrow {}^{235}U + {}^{4}He \quad \lambda = 24\,390$ years
- ${}^{240}Pu \rightarrow {}^{236}U + {}^{4}He \quad \lambda = 6580$ years
- ${}^{241}Pu \rightarrow {}^{241}Am + \beta \quad \lambda = 15$ years
- ${}^{241}Am \rightarrow {}^{237}Np + {}^{4}He \quad \lambda = 432$ years

Each reaction leads to the creation of around 2500 Frenkel pairs induced mainly by the uranium displacement cascade at 86 keV. Stable defects created at the atomic scale can then diffuse and affect macroscopic properties.

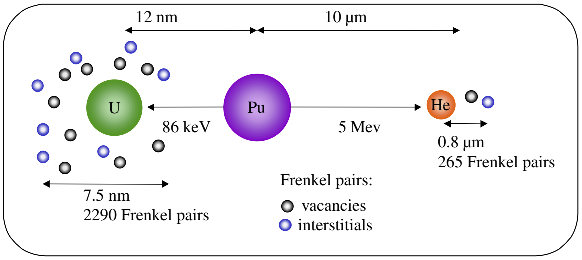

Fig. 4. Plutonium decay and the generation of defects.

As a result, we have to consider:

- Radiation damage due to the emission of high energy particles inside the bulk of the material: displacement of atoms, creation of defects (vacancies, interstitials), of dislocations and voids.
- Creation of gas impurities: helium. Whereas helium is chemically inert, it is known to be insoluble in metals due to the fact that its electronic band is full. It can aggregate in the form of He-vacancies clusters or bubbles and in some cases can induce bulk swelling or intergranular embrittlement.
- Increase in impurities: americium, neptunium, uranium; whereas americium stabilizes δ-phase, neptunium and uranium have the contrary effect. So the chemical changes could induce a change in the phase stability for δ plutonium alloys which are metastable at room temperature as discussed previously.
- Change in mechanical properties.

3. Swelling in plutonium alloys

Swelling in plutonium alloys is the most striking effect of self radiation. It has been studied both experimentally by XRD for different alloys, Pu–Ga and Pu–Al, especially by Chebotarev and Utkina [4] and Ellinger et al. [3].

The main conclusions are: the swelling saturates approximately after 0.2 dpa and the saturation swelling increases linearly with the deltagen alloying content.

Ellinger also has determined the contribution of americium to the global swelling by the following relation: $a(A) = 4.6405 + 0.0034[\mathrm{Am}]$, up for a maximum concentration of 15%.

There has been early modelling of the phenomenon by Wolfer and Wehner [5,6]. More recent works by Wolfer and Schwartz have proposed a model taking into account the rate of generation of helium, the total concentration of helium, the number of helium bubbles, the diffusion of helium versus time [7,8]. They have thus obtained the evolution of the concentration of helium in solution and the concentration of bubbles versus time as shown in Fig. 5. These values have been compared to results of TEM characterization, so as to determine the ratio helium on vacancy which is close to 2. The result of this comparison is given in Fig. 6, for an activation energy for helium migration of 0.72 eV. There is a rather good agreement between the theory and the experimental results.

4. Plutonium sample preparation

In order to conduct this study, plutonium–gallium alloys stabilized with gallium content of 1.9 at.% have been cast by gravity. The samples are then machined to the desired dimensions. The required geometry for high temperature dilatometry is a cylinder of 6 mm in diameter and whose height is also 6 mm. For optical fiber dilatometry, the cylinder is 5 mm in diameter and 10 mm height. For XRD analyses, the diameter of the samples is 10 mm and the thickness is 2 mm. They have then undergone a heat treatment of 10 h at 460 °C under

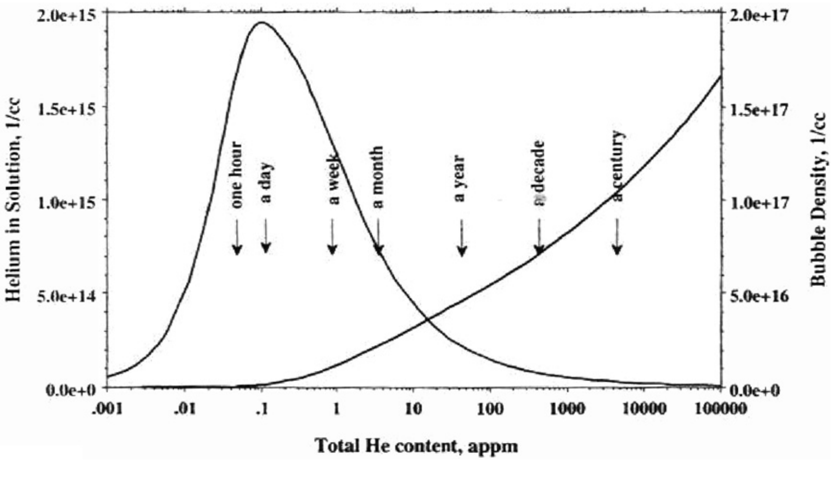

Fig. 5. Simulation of helium in solution and bubble density as a function of time or helium content determined by the model of Wolfer [5].

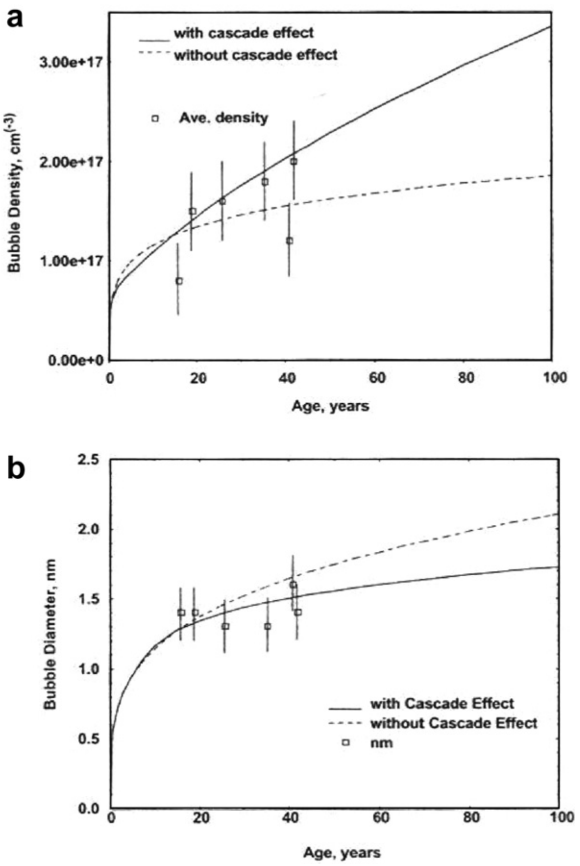

Fig. 6. (a) Predicted helium bubble density and (b) average bubble diameter as a function of the plutonium age or the helium content [7,8].

high vacuum (2×10^{-7} mbar) to just partially homogenize the gallium distribution and to ensure that all samples are δ-monophased.

5. Plutonium sample characterization

The plutonium samples have been characterized for this study by using two methods that give measurements of the swelling: dilatometry (both high temperature and optical fibre) and X-ray diffraction.

5.1. High temperature dilatometry

The first way to measure the swelling of plutonium is the high temperature dilatometry. The expansion of a sample is measured by doing a cycle from room temperature up to 360 °C at 10 °C/h, there is no holding time at 360 °C, and then the temperature is decreased to room temperature at 10 °C/h. This cycle corresponds to the restoration of the crystalline structure, which is considered to be ended at 300 °C. The maximum temperature of 360 °C is thus well above this annealing temperature. After the first cycle, a second one is made in the same conditions. There is no waiting time between runs 1 and 2. Such a procedure is used so at to be sure that the crystalline structure has been restored and that no new cascade has created new defects such as vacancies or interstitials. By doing the difference between first and second run which is related to the restoration of the defects, we can obtain the influence of vacancies and interstitials on the swelling of the sample. This measure is made at 300 °C, and the difference at that temperature $\Delta l1-\Delta l2$ is representative of the dilatation induced by these vacancies and interstitials. It is then possible to follow the evolution of the swelling versus time by doing this kind of measurement once a

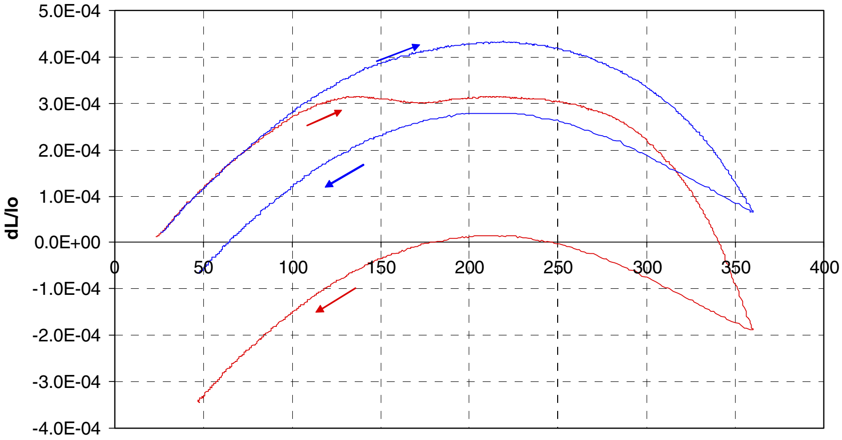

Fig. 7. Results of high temperature dilatometry measurement on a plutonium–gallium alloy sample, stored at ambient temperature, heated at 10 °C/h up to 300 °C, with no holding time, and cooled at 10 °C/h down to room temperature. (For interpretation of this figure, the reader is referred to the web version of this article.)

month at the beginning, then at longer time. The major drawback of this technique is that it gives only one value per sample; the conditions in which the sample is stored must be monitored so as to correlate the results with the history of the sample: in our case, all the samples are stored at ambient temperature. The accuracy of the measurement is given by calibration over the temperature range: it is currently 3×10^{-5}. A typical curve is given in Fig. 7. The red curve is the first run and the blue one is the second. It can be clearly seen that the crystalline structure is restored between 100 and 300 °C. Several experiments were performed at different time expressed in dpa (displacements per atom; in our case it is about 0.1 dpa a year), which respectively give a swelling of 68, 38, 110 and 126×10^{-6} for 0.02, 0.04, 0.18, and 0.3 dpa.

5.2. Optical fibre dilatometry

Since only one value per sample is available for high temperature dilatometry, another experimental device has been developed in order to continuously measure the swelling of our samples versus time. The choice has been made to monitor the evolution of the length of the sample at a given temperature. For doing that, we have equipped the sample with an optical fibre containing three Bragg grating network as shown in Fig. 8 [9]. The sample is machined in order to make notches along its height. The fibre containing the Bragg grating networks is glued in these notches so that one Bragg grating network in on one side of the sample and the second one is on the other side. The third network is independent of the sample. A laser wave is put into the fibre and the networks give information of the length of the network. When the temperature varies or when the sample endures swelling, the network length will change and so will the signal it gives. The third network gives a calibration, which helps to correct the temperature variation or the pressure change for example.

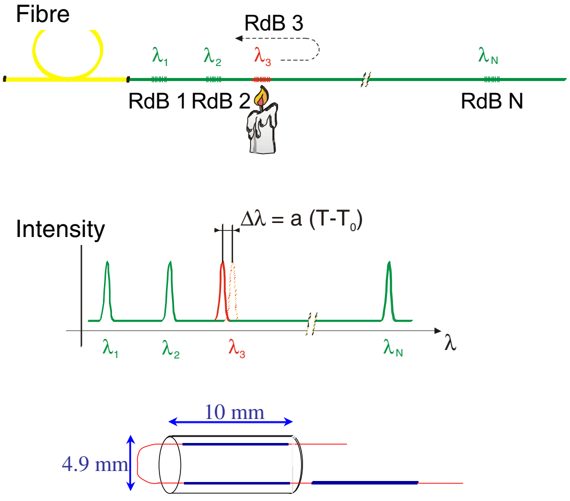

Fig. 8. Instrumentation of a sample of plutonium–gallium alloy for optical fibre dilatometry: the optical fibre is in red and the Bragg grating networks are in blue. (For interpretation of this figure, the reader is referred to the web version of this article.)

Before the experiment, an initial heat treatment is made for 10 h at 360 °C under high vacuum in order

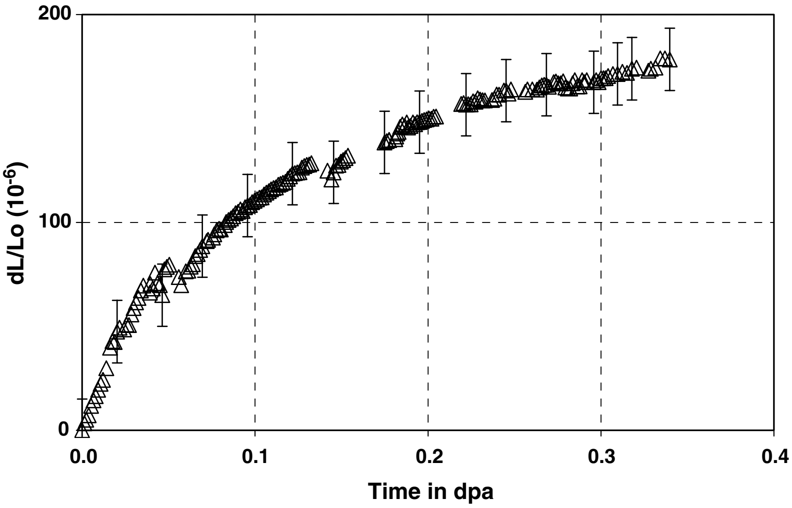

Fig. 9. Result of swelling of a plutonium–gallium sample versus time by optical fibre dilatometry.

to restore the crystalline structure. The sample is then put in a furnace at a constant temperature. It is thus possible to measure continuously the length and the temperature of the sample. The result is shown in Fig. 9: it gives the evolution of $\Delta l/l0$ versus time expressed in dpa. It can be seen that: first, there is a transient evolution up to 0.2 dpa, followed by a linear evolution. These are first results that must be confirmed by further data. But there are very promising and as the temperature is fixed, it will be possible to change it and see its effect.

5.3. X-ray diffraction

Another way to follow the evolution of the swelling is to measure the lattice parameter versus time [10–12]. XRD experiments were performed using a classical $\theta/2\theta$ diffractometer (Brüker D8 Advance) with copper radiation. XRD analyses were performed in the reflection mode and the used detector was a positive sensitive detector (Braun), integrating an angular range of 6°, with a 12 μm thick nickel foil used to remove the Kβ radiation. The diffraction diagrams were recorded at room temperature with a step time of 0.3 s and a step size of 0.015° from 30 up to 130° in 2θ angle.

The initial lattice parameter is called $a_{\text{reference}}$. Then the lattice parameter is measured at different times and is called a_{aged}. The lattice swelling is defined as:

$$\Delta a/a = (a_{\text{aged}} - a_{\text{reference}})/a_{\text{reference}}.$$

Before each XRD analysis, samples were electropolished under a tension of 40 V in a cooled bath at 266 K composed of 90% ethylene glycol and 10% nitric acid to remove surface oxides and other possible impurities. Then, samples were stored under vacuum between each XRD analysis. The whole plutonium handling was performed in a glove box with a circulating nitrogen supply. The diagrams of diffraction are presented in Fig. 10 and reveal the presence of δ-monophased alloys and show that the peaks tend to go to lower θ value with aging. The evolution versus time of the lattice swelling as well as a curve fitting based on the following relation:

$$\Delta a/a = a(1 - \exp(-bt)),$$

where a is the lattice swelling amplitude at saturation and b a factor corresponding to the lattice swelling kinetics is given in Fig. 11. The trend shows

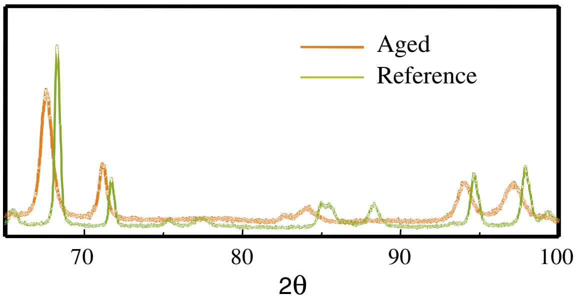

Fig. 10. X-ray diffraction spectra obtained for a reference and aged samples of plutonium–gallium alloy showing the evolution of the peaks versus time.

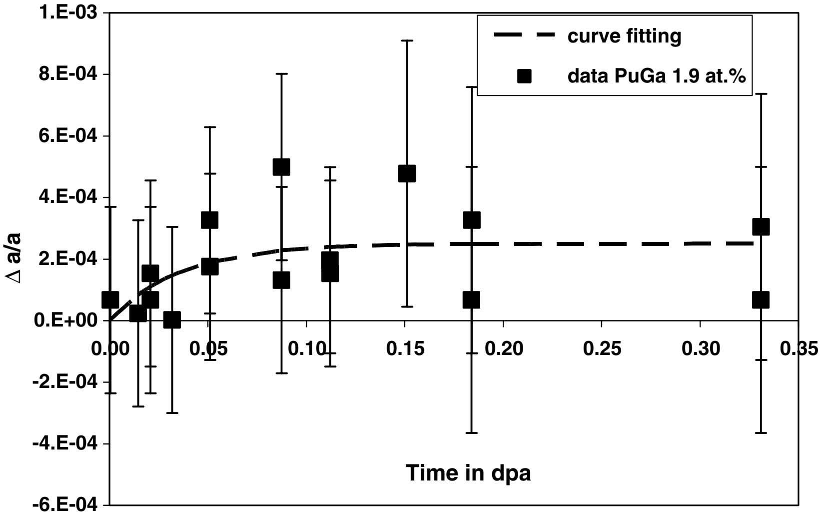

Fig. 11. Evolution of the lattice parameter versus time expressed in dpa for the plutonium–gallium 1.9 at.% alloy as measured by X-ray diffraction.

an increase from the early beginning up to 0.1 dpa from which it tends to saturate.

6. Discussion

Fig. 12 gathers the swelling measurements obtained by the three different techniques, and leads to the following comments:

- The value obtained with high temperature dilatometry and optical fibre dilatometry are in good agreement: then, after the transient evolution (first part of the curve) the trend shows a slow increase for both experiments.
- According to the curve fitting of the values obtained by X-ray diffraction, the lattice swelling seems to increase up to 0.1 dpa and then saturates to reach a lattice swelling of about 250×10^{-6}. This lattice swelling has to be considered with care regarding the accuracy of the values of lattice parameter compared with the amplitude of lattice swelling. A discrepancy can be observed between the results obtained by XRD and dilatometry since the microscopic swelling would appear higher than the macroscopic one as the total swelling measured by dilatometry is the sum of the lattice and helium swellings and voids formation.

However, we have to consider the fact that the temperature is not exactly the same for all the samples: the temperature is set constant in the oven containing the sample with the optical fibre, whereas the other samples used for high temperature dilatometry and XRD are just kept in glove boxes ambiance. A correction should be made in order to correct the values. This will be done when modelling of all the phenomena will be appropriate. But the modelling will be very accurate if we want to explain the difference which is seen between dilatometry and XRD.

The results presented by Schwartz et al. [8] show the presence of helium bubbles on a 18 years old plutonium sample. Their results show also an increase in the number of bubbles and not of the size of these bubbles. These bubbles certainly play a role in swelling that we can not determine clearly in XRD. We should be able to measure the influence of the helium bubbles in optical fibre dilatometry but we do not have enough measurement time up to now.

It is not possible to compare exactly the results of this study with the results of Schwartz et al. as the content of impurities of their sample is possibly not the same and in the same order of magnitude. In order to conclude, we should make some measurement on a TEM in order to determine how

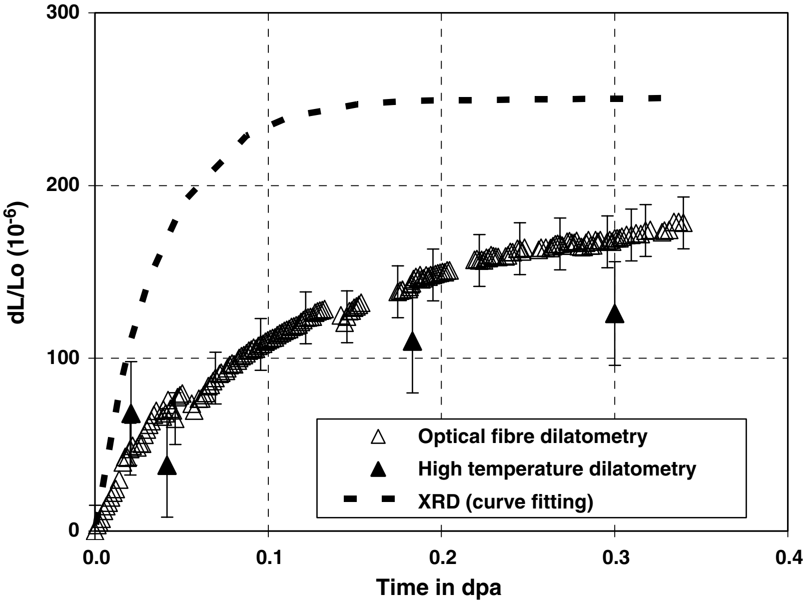

Fig. 12. Comparison of the results of the swelling of a plutonium–1.9 at.% gallium as measured by XRD and high temperature dilatometry and optical fibre dilatometry.

helium migrates and eventually contributes to clusters formation.

All these results give contradictory evolution possibilities: up to now, the swelling is low and tends to saturate quite rapidly. But the tendency is not so sure for the results obtained with optical fibre dilatometry which seems to be a promising experiment.

7. Conclusion

This study shows a low increase of the swelling of the plutonium–1.9 at.% gallium alloy versus time up to 0.2 dpa as measured by dilatometry. Results deduced from X-ray diffraction seem to show a lattice swelling which would saturate from 0.1 dpa even if this lattice swelling is of the same order of magnitude than the accuracy of XRD. A specific study was performed on lattice swelling induced by self-irradiation for cored and homogenized PuGa alloys and more results will be discussed more in detail in a next article [12].

We have thus to continue the measurements in order to better understand what is going on, try to make other kind of measurements and obtain more data especially with the optical fibre dilatometry.

We can also try to model the phenomena in order to predict aging effects on properties of plutonium alloys. The approach is to identify key materials properties, characterize properties of plutonium alloys at initial time, measure the effect of aging on key properties and finally refine models. This modelling is based on three scales from atomic to mesoscopic scales: ab initio calculations, molecular dynamic calculations and mesoscopic calculations both with standard rate theory and Monte Carlo calculations [13].

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