ESRF	**Experiment title:** Delta-phase stabilization in Pu(x)Al(1-x)alloys as studied by high-energy XRD and PDF-analysis	**Experiment number**: HS-2880
Beamline: ID15B	**Date of experiment**: from: 22th February 2006 to: 26th February 2006	**Date of report**: 1st August 2006
Shifts: 15	**Local contact(s)**: Dr. Veijo Honkimaki, Dr. Gabriela Gonzales Aviles	*Received at ESRF:*

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Report:

The delta-phase of plutonium (face-centered cubic) is stable between 319°C and 451°C but can be retained at room temperature by alloying plutonium with delta-phase stabilizer elements (gallium, aluminum, americium, cerium…). The stability of the delta-phase can be strongly affected by a variation of parameters such as the delta-phase stabilizer concentration, the metallurgical state of the alloy, the temperature or the pressure [1,2]. The mechanisms for delta-phase stabilization in plutonium alloys have been widely studied but they are still not well understood: they are known to be strongly related to the 5f electrons of the plutonium atoms and thus to the local atomic arrangement in the Pu-alloys since their electronic structure is directly related to their crystalline structure [1,2]. In order to study the delta-phase stability in plutonium-aluminum alloys, XTS experiments (X-ray Total Scattering) have been performed at ESRF and XTS-patterns have been analyzed using the PDF-method (Pair Distribution Function) [3] in an attempt to characterize the local atomic arrangement in the alloys.

The investigated materials are Pu-Al alloys with various aluminum contents (1.8, 2.3, 3.0 and 5.8 at%Al) and for two distinct metallurgical states (as-cast and homogenized). As-cast samples are considered as segregated (*i.e.* their grains are cored) whereas the homogenized samples have undergone a heat treatment of 200 hours at 450°C. After electropolishing to remove surface oxides and other possible impurities, samples were confined between two Kapton® foils to avoid contamination.

XTS-experiments in the transmission geometry have been carried out at room temperature on Pu-Al samples. The beamline ID15B was chosen because it makes available to work with a high energy incident beam of about 90 keV ($\lambda \sim 0.14$ Å). It is particularly suitable for PDF-analysis because the related high reciprocal wave vector Q_{max} of about 90 $Å^{-1}$ corresponds to a low probing distance r_{min} of about 0.07 Å, allowing thus to study the local atomic arrangement in the plutonium-aluminum alloys. The measurement-time was particularly short (~10 s) since a 2D-image plate detector MAR345 was used. Taking into account corrections such as absorption, polarization, Compton and multiple scattering… the 2D-images were first transformed into scattering patterns $I^N(2\theta)$ and subsequently PDF-curves G(r) were computed using the PDFgetX2 software [3,4].

XTS scattering patterns are composed of both diffraction and diffuse scattering patterns. Lattice parameters are determined from a Rietveld refinement carried out in *Fm3m* space group. Results are in good agreement with the literature [1,2,5]. The lattice parameter of the delta-phase decreases with increasing aluminum concentrations. But the decrease is more severe than predicted by the Vegard law, showing a contraction of the cubic lattice that is more important than expected. The "over-contraction" of the cubic lattice is often associated to an overlapping of the 5f orbitals of the Pu-atoms yielding thus a reduction of the atomic volume of plutonium (the 5f electrons become itinerant instead of localized). On the other hand, the more aluminum atoms in the Pu-Al alloys, the more strains inside the cubic lattice; subsequently, the more atomic disorder should be observed. Bragg peaks provide useful information about the long-range order but no significant differences are observed when varying the Al-concentration. Therefore, the short-range order must be probed. Diffuse scattering originates from the atoms that are not located at the position expected in an ideal crystal. So, details about the local atomic arrangement are awaited from the PDF-analysis of the XTS-data.

Figure 1 exhibits the PDF-curves G(r) for the homogenized Pu-Al samples. The peaks noted *CS1* to *CS11* (*CSi* stands for *Coordination Shell number i*) correspond to interatomic distances between plutonium and aluminum atoms in the face-centered cubic lattice. Conversely, some extra peaks can not be attributed to the cubic structure (red arrows on Figure 1) even though it is the only structure deduced from the diffraction patterns refined using the Rietveld-method. Equivalent observations are made for the as-cast samples. In view of that, assumption was made that the extra peaks could be a signature of other plutonium compounds such as:

- intermetallic precipitates owing to the presence of impurities like iron and nickel [6],
- plutonium oxides since the permeability of Kapton® to oxygen is not zero,
- other phases: the monoclinic alpha phase of plutonium if the depletion in aluminum is locally low enough, the body-centered cubic epsilon-phase in case of quick cooling during the elaboration process, or a "new phase" labeled sigma that has only been observed by Conradson for Pu-Ga alloys containing from 1.70 at %Ga up to 3.35 at %Ga [7,8].

Finally, the only compound providing interatomic distances that seem to match the extra peaks observed on the PDF-curves is the so-called sigma-phase. Conradson assumes the sigma-phase to be organized in nano-domains acting as precursors for a martensitic transformation in case of a temperature decrease [7,8], but this last assumption is in contradiction with our electrical resistivity measurements on the Pu-Al alloys since they show that the PuAl5.8 alloy does not undergo any martensitic transformation. In conclusion, the question is that whether the extra peaks are not related to the sigma structure or that the assumption of Conradson about the role of the sigma-phase is wrong.

Prospectively, EXAFS experiments at the L_{III}-edge of plutonium are expected to complete this work on plutonium-aluminum alloys at the beamline BM20-ROBL dedicated to the analysis of actinide materials by using EXAFS. Absorption experiments would allow confirming the presence of the extra peaks with a greater accuracy in the low-*r* range (< 5 Å).

The results reported here have been presented on a poster during the international conference "Pu Futures The Science" at Asilomar, Pacific Grove, CA, USA (July 9th-13th 2006) and they will be further discussed in a subsequent publication.

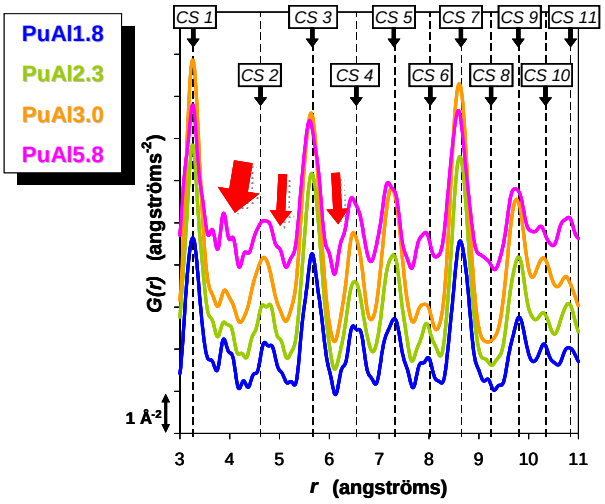

Figure 1. PDF-curves for the homogenized Pu-Al samples computed using the program PDFgetX2 [4,5]. Coordination shells related to face-centered cubic structure of the delta-phase are labeled *CS1* to *CS11*. Red arrows show extra peaks that can not be attributed to oxides (PuO, PuO_2, Pu_2O_3…) nor intermetallic compounds (Pu_6Fe…) nor the alpha- or epsilon-phases but to the sigma structure described by Conradson [7,8].

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