Utilization of Principal Component Analysis on Plutonium EXAFS Data from the Advanced Photon Source

Jeff Terry,
Roland K. Schulze,
Thomas G. Zocco,
J. Doug Farr,
Jeff Archuleta,
Mike Ramos,
Ray Martinez,
Barbara Martinez,
Ramiro Pereyra,
Jason Lashley
Los Alamos National Laboratory, Los Alamos, NM 87545, USA
Steve Wasserman,
Mark Antonio,
Suntharalingam Skanthakumar,
Lynne Soderholm
Argonne National Laboratory, Argonne, IL 60439, USA

Since the 1941 discovery of plutonium (Pu) by Glenn Seaborg, this enigmatic metal has been the subject of intense scientific investigation. Despite these efforts, there is still much to be learned about the unusual physical and mechanical properties of plutonium and its alloys. In particular, unalloyed Pu undergoes six allotropic phase transformations upon cooling from the melt to room temperature. Many of these phase transformations result in large volume changes and produce low-symmetry crystal structures. These unusual characteristics have made the metallurgy of Pu and Pu alloys particularly challenging. For example, the highest density allotrope, α (monoclinic), is extremely brittle and oxidizes readily, making it a poor choice for manufacturing operations. The addition of 1 wt. % Ga stabilizes the face-centered cubic δ structure, α phase with vastly superior mechanical properties when compared to α-Pu. Phase relations within the Pu-Ga system have been studied in detail, providing an initial basis for the understanding of the metallurgical properties of the system.

However, a fundamental gap exists in our understanding of bonding properties of δ-phase Pu that has been stabilized by alloying. Most simply stated:

> What is the local atomic environment of the plutonium atoms?
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> Does the local environment change as a function of concentration?
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> Does the local environment change as a function of alloying agent?
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> What is the local atomic environment of the alloying agent?

At present, there is a substantial controversy over the local structure of Pu alloys stabilized into the face-centered cubic structure (δ-phase) by alloying with Ga. The local structure can be determined in several different ways: one is to calculate pair distribution functions (PDFs) from either neutron or x-ray scattering data, while the other is to calculate the local structure from the extended x-ray absorption fine structure (EXAFS). The controversy is that the EXAFS work exhibits a high frequency oscillation, corresponding to a longer bond length than would be expected in the fcc phase. Furthermore, no unexpected peaks appear in the PDFs obtained from neutron scattering. The former represents data exploring a region to a depth of approximately 6μ, while the latter explores the "bulk" structure. The long bond length peak observed in the EXAFS spectrum has been subject to many different explanations, ranging from the formation of a secondary phase with a body-centered cubic structure to the formation of an oxide layer. Recent EXAFS measurement at the Advanced Photon Source (APS) by Jeff Terry and Lynne Soderholm have shown that an oxide layer cannot be responsible for this unattributed peak. Those measurements utilized well characterized samples in order to understand the effects of sample cleanliness and utilized probes with different sampling depths (by using both electron yield and fluorescence detection). Unfortunately, due to a monochromator problem, it was not possible to identify conclusively the origin of the unknown peak. Resolution of this controversy is important to gain an understanding of the structure of Pu alloys.

The area of focus in this proposal is the Pu-rich portion of the phase diagram. Samples will be prepared around the minimum concentration necessary to stabilize the δ-phase. In order to determine the local atomic environment of the pluto-

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