Plutonium metallurgy: The materials science challenges bridging condensed-matter physics and chemistry

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Abstract

Although there exists evidence of metallurgical practices dating back over 6000 years, studies of Pu and Pu alloys have been conducted for barely 60 years. During the time of the Manhattan Project and extending for some time afterward, the priority to produce the metal took precedence over the fundamental understanding of the metallurgical principals. In the past decade or so, there has been a resurgence in the basic metallurgy, condensed-matter physics, and chemistry of Pu and Pu alloys. These communities have made substantial progress, both experimentally and theoretically in many areas; however, many challenges still remain. The intent of this brief overview is to highlight a number important challenges that we face in the metallurgy of Pu including phase transformations and phase stability, aging, and the connection between electronic structure and metallurgy.
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1. Introduction

The origins of metallurgy have been traced back to the highlands of western Asia, northwest of the Persian Gulf, as early as the year 4300 BC [1]. By 2000 BC, smelting, melting, casting, annealing, and forming of metals such as gold, silver, copper, tin, lead, and iron had been practiced. Between 2000 BC and 1800 AD, advances in metallurgy clearly impacted society in many major ways in the arts, agriculture, industry, and military applications. The Bronze Age gave way to the Iron Age and by the beginning of the 19th century, the industrial need for steel drove metallurgy to become an important discipline connecting chemistry, physics, and mechanics. Matthiessen's rule, based on an 1867 electrical conductivity investigation, is credited as the beginning of the "physics of metals", solid-state physics, and now condensed-matter physics. Phase diagram investigations, the development of the constitution of alloys, and the principles of heterogeneous equilibria by Willard Gibbs were first published in 1876. Around the same time, physical chemistry was laying the basis for the study of phase transformation kinetics. By the end of the nineteenth century, metallurgy had established its role in the inter-space between condensed-matter physics, chemistry, and crystallography.

During the twentieth century, tremendous advances in metallurgy were made possible by von Laue's (1912) discovery of the diffraction of X-rays and the subsequent developments by Bragg and others in the studies of crystal structures. This technology opened the door to crystallographic and microstructural studies of metals and alloys and the discovery of superlattice structures, Hume-Rothery alloys, Laves compounds, and the importance of point defects. Furthermore, significant developments in the understanding of solidification, nucleation and growth theory, plasticity, texture, failure, martensitic phase transformations, diffusion, and many other physical and mechanical properties of metals and alloys were made. Scientific advances in physical metallurgy clarified our understanding that processing of metals and alloys is responsible for setting the microstructure, and that the microstructure is closely related to the performance of materials. Microstructure–properties–processing–theory relationships will undoubtedly continue to be the central component of 21st century materials science.

The understanding of metallurgy gained over the previous centuries created a fundamental base for learning and understanding how to process and characterize the new element plutonium when it was created by Seaborg, Kennedy, and Wahl in 1940 [2]. The earliest stages in Pu metallurgy were motivated

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by the need to produce a product; at that time, quantity took precedence over quality, and thus much of the basic science was left untouched. Problems with consistent density and phase transformations led C.S. Smith to suggest that intentionally alloying of Pu may be the answer and ultimately, an alloy of 3.0–3.5 atomic percent Ga was used in the Trinity test [3]. From 1945 onward, a tremendous amount of effort was placed on determining phase diagrams and phase stability of the actinide metals. Bochvar et al. [4], Ellinger et al. [5], Zachariasen and Ellinger [6], Chebotarev et al. [7], Orme et al. [8], Timofeeva [9], Hecker and Timofeeva [10] and many others contributed significantly to the understanding of the crystal structures, phase diagrams, and phase stability of Pu and its alloys.

In the last two decades, the motivation for Pu science has somewhat shifted. No longer is the sole purpose to produce a particular product. Rather, the need is to understand the fundamental underpinning of properties. In addition, the problem of aging of Pu has dictated much of the science being now developed [11,12]. The continuous radioactive decay of Pu produces an array of impurity daughter products that accumulate with age. How the damage introduced by radioactive decay and the resulting impurities affect metallurgical aspects of Pu, such as phase transformations and magnetic properties, are areas of intense research. Today, Pu science is mainly focused on the understanding of the fundamental relationships between electronic structure, crystallographic aspects, phase stability, and the roles of microstructure, impurities, and defects.

The boundaries between metallurgy, condensed-matter physics, and physical chemistry in the study of Pu are now overlapped more than ever. Recent advances in our understanding of this intriguing material are being made in all areas of physical science. This overview will highlight a number of these exciting advances and will focus on the significant challenges in the field of Pu metallurgy. Among the topics to be discussed are phase transformations and phase stability, metallurgical consequences of aging, and the important connection between electronic structure and materials physics. Substantial advances have been made in our understanding of the phase diagram, but details of the thermodynamics and kinetics of low temperature transformations, particularly below ambient, remain unclear. Advances have been made in our knowledge of the $\delta \rightarrow \alpha'$ isothermal martensitic transformation [13–16], but still much is unknown about the atomistic mechanisms and kinetics of this transformation during temperature or pressure excursions. Even after 30+ years, the origin of the double-C kinetics in the published time-temperature-transformation (TTT) diagram remains essentially unresolved. Natural aging of Pu has been the focus of significant recent efforts [17], but we still do not fully understand the basis of such features as the lattice parameter expansion with time, the volume increase which can be significantly different from that expected from the lattice parameter expansion, the vacancy migration energy, or the mechanism that appears to limit the size of the helium bubbles that form from alpha decay of Pu into U and He. The connections between the electronic structure, lattice dynamics, and microstructural details continue to present a significant challenge.

With many years of accumulated metallurgical knowledge about almost every element in the periodic table, we substantially understand most metals. Hopefully, research during the 21st century will help to eliminate many of the still perplexing details of the deeply complex structure–properties–processing relations in Pu. This is a very exciting time to be engaged in Pu metallurgy. With ever-improving computational capabilities and significant focus on electronic structure calculations and experiments, there are now collaborative worldwide efforts to advance our understanding.

2. Phase transformations and phase stability

For decades, researchers in the West followed the published Pu–Ga phase diagram developed by Ellinger et al. that indicated a region of face-centered cubic δ phase stability, extending to sub-ambient temperatures, for Ga contents between approximately 2 and 9 at.% [5]. During this same time, following the phase diagram studies by Chebotarov et al. [7], researchers in the former Soviet Union considered the possibility that the δ phase is only metastable at ambient temperatures, and, if it were not for exceedingly slow kinetics, would decompose via a eutectoid reaction to the monoclinic α phase and the compound Pu_3Ga. Although the Chebotarov et al. phase diagram showing the eutectoid [7], and the calculation by Adler in 1991 [18] of a eutectoid transformation that essentially confirmed this were available in the West, it was only after the Hecker and Timofeeva publication "A Tale of Two Diagrams" in Los Alamos Science in the year 2000 [10] that increasing worldwide consensus on the eutectoid decomposition has developed. The phase diagram calculations by Adler using the FACT program [18], by Baskes et al. using a modified embedded atom method potential within a molecular dynamics simulation [19], and by Turchi et al. using the CALPHAD program [20] have predicted the eutectoid reaction. The Third Law of Thermodynamics also dictates that a wide solubility δ phase is unlikely to be stable at temperatures near 0 K [21,22].

The thermodynamic details of the phase diagram, dictated by the free energy of the phases as a function of temperature and composition, also play a prominent role in the low temperature $\delta \rightarrow \alpha'$ transformation [22]. In the most simplistic of terms, the thermodynamics dictates the lowest energy phase, but the activation barrier between the phases along the transformation path will control the kinetics of the phase transformation.

Plutonium alloys are notoriously inhomogeneous. The sharp decline in the $\delta \rightarrow \alpha'$ transformation temperature with increasing Ga content means that an inhomogeneous alloy could transform over a wide range of temperatures that vary significantly from the martensite start temperature for the average composition. Therefore, it is important to understand how to thoroughly homogenize the material. Early studies on the homogenization of δ phase alloys demonstrated the importance of time at temperature in equilibrating the Ga concentration inhomogeneities across the grains [23]. The diffusion of Ga in ε-Pu is rapid, with a diffusion coefficient $D \sim 10^{-8}$ to 10^{-7} cm^2/s. This compares with the much lower diffusion coefficient of Ga in the δ-Pu, $D \sim 10^{-14}$ to 10^{-11} cm^2/s [24].