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The Melt-Dilute Treatment of Al-Base Highly Enriched DOE Spent Nuclear Fuels: Principles and Practices

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Abstract

The melt-dilute treatment technology program is focused on the development and implementation of a treatment technology for diluting highly enriched (>20% ^{235}U) aluminum spent nuclear fuel to low enriched levels (<20% ^{235}U) and qualifying the LEU Al-SNF form for geologic repository storage. In order to reduce the enrichment of these assemblies prior to ultimate geologic repository disposal, the melt-dilute technology proposes to melt these SNF assemblies and then dilute with additions of depleted uranium. The benefits accrued from this treatment process include the potential for significant volume reduction, reduced criticality potential, and the potential for enhanced SNF form characteristics. The emphasis within the development program to date has been on determining the process metallurgy and off-gas system design for the treatment of all types of Al SNF (UAl_x, Al-U_3O_8, and Al-U_3Si_2). In determining the process metallurgy a wide range of alloys, representative of those expected in the Al-SNF form, have been fabricated and their product characteristics, namely microstructure, homogeneity, phase composition, and "ternary" constituent effects have been analyzed. As a result of the presence of species within the melt which will possess significant vapor pressures in the desired operating temperature range an off-gas system is necessary. Of the volatile species the one of greatest concern is ^{137}Cs.

Introduction

Aluminum-base spent nuclear fuel (SNF) assemblies from foreign and domestic research reactors are owned by the Department of Energy (DOE) and will be sent to the Savannah River Site (SRS), prepared for interim storage, and eventually sent for geologic storage at Yucca Mountain, Nevada. Aluminum-base research reactor fuel represents only about 1% of the total SNF that is to be stored in the geologic repository. During the next 30-40 years, SRS expects to receive and store approximately 42 metric tons of heavy metal (MTHM) of spent nuclear fuel. This material will be treated and dry stored in a "road ready" form until the repository is open. About three quarters of the fuel by volume is in the form of high-enriched uranium (HEU) and may present criticality control issues while storage that are not present for low enriched (LEU) fuel disposition.

Research reactor fuels are fabricated using either an aluminum-uranium alloy or mixtures of aluminum and uranium aluminides, uranium silicides or uranium oxide powders. Originally, highly enriched uranium (93% ^{235}U) was used in fuel plate fabrication. The four fuel types, mentioned above, are manufactured in various size,

shape, and structural configurations. However, many research reactor fuel assembly designs are of the material test reactor (MTR) type. They are irradiated to various burnups, and some assemblies have been stored in water for up to 30 years after discharge from the reactor. Once the SNF assemblies have been returned to SRS, they must be put into a form for site interim storage and for eventual long term geologic storage.

The melt-dilute process is a method of preparing DOE spent nuclear fuel for long term storage. The process melts the fuel assemblies to reduce their volume and alloys depleted uranium to isotopically dilute the U^{235} concentration and reduce the potential for criticality and proliferation concerns. The resulting alloy is cast into a form for long term geologic repository storage. Benefits accrued from the melt-dilute process include the potential for significant volume reduction; reduced criticality potential, and potential for enhanced SNF form characteristics.

Experimental

Fundamental experimental investigations of the solidification microstructure resulting from different processing treatments have been carried out in order to provide information for the development of the melt and dilute processing technology for U-Al, UAl_x, U-Si, and Al-U_3O_8 research test reactor fuel assemblies. Development of ternary isothermal sections for the U-Al-Si fuels using the standard Gibbs triangulation technique and fundamental thermodynamic calculations assessing the possible reaction paths in the U-Al-O system have been performed. Additionally, fundamental dissolution kinetic experiments using depleted U_3O_8 and U_3Si/U_3Si_2 samples and molten aluminum have been conducted. Additionally preliminary experiments have been conducted to evaluate the partitioning of "ternary" species during solidification and the volatility of ternary species and methods to effect their capture.

Results and Discussion

UAl_x Fuels and Alloys

At present, the majority of the spent research reactor fuels are aluminum-uranium type. After irradiation, the fuel plates contain primarily aluminum, enriched uranium, and various fission products. The concentration of the fission products is relatively low; so process metallurgy can be discussed using the basic uranium-aluminum phase diagram shown in Figure 1. When as received SNF assemblies are melted, the compositional range is expected to vary from about 3 to 10 wt% uranium.

From the phase diagram, a single liquid phase exists above 660°C for alloys containing uranium contents less than the eutectic composition (13.2 wt% uranium). The eutectic provides the lowest liquidus temperature, and at the eutectic composition, the liquid to solid transformation occurs at a constant temperature, thereby, eliminating gravity segregation of a primary phase. Operating the process below 850°C and above 646°C and at the eutectic composition affords ideal process conditions. Additionally, low process temperatures reduce the amount of fission products released as off-gas because of the low vapor pressure of various species.

Figure 1. (A) Uranium-Aluminum Binary Phase Diagram[1] (B) Near Eutectic (~ 13.2wt%U) Alloy

U-Al-Si Fuels and Alloys

The United States Reduced Enrichment Research and Test Reactor program operated by Argonne National Laboratory has worked for the past 15 years to develop low enriched (<20%) uranium alloy fuel for use in research and test reactors. The main driver for this program is the development of non-proliferable nuclear fuels.

The alloy system that has met with the greatest success is the U-Si binary system. Currently U-Al-Si alloy fuels are in use in France, Germany and Japan. They are expected to be approximately 20% of the fuel inventory to be treated by the melt-dilute process.[2]

Typically, melting of a U-Al-Si fuel assembly will result in a melt-composition in the range of approximately 1-10 wt% uranium, 1 wt% Si and 89-98 wt% Al for the various MTR assemblies. For the melt-dilute process, alloy composition is the main driver for treatment temperatures. For a ternary U-Al-Si alloy in the indicated concentration range, little if any ternary liquidus information is available. The only published data available indicates a liquidus temperature between 660°C and 950°C for an alloy with this composition.[3] Thus, in order to determine a more accurate melting/liquidus composition ternary isothermal section through the U-Al-Si ternary T-X diagram were constructed using the Gibbs triangulation method and experimental data. Ternary isothermal sections from 500-800°C are depicted in Figure 2 and show the relative position of the expected fuel composition within the phase fields as temperature increases. From these isothermal section it can be seen that a typical 90Al-9U-1Si alloy will be fully molten at 800°C.

A further concern with the treatment of the silicide fuel with respect to treatment cycle adaptations is the kinetics of dissolution of the uranium silicide intermetallic particle (USi_3 and U_3Si_2) in molten aluminum at temperatures below 1000°C. Dissolution of the intermetallic particles will occur by the following reaction:

$$U_3Si_2 + Al \text{ ^ } U\ (Si, Al)_3 + Al$$

Experiments were conducted to evaluate the forward reaction kinetics of this reaction in the desired treatment cycle temperature range. Depleted U_3Si_2 powder was added to molten aluminum at 850°C. The overall U-Al-Si alloy composition that would be expected assuming all of the silicide powder was reacted was approximately equal to the expected fuel composition (90Al-9U-1Si). Figure 3 displays the metallographic results from the sample heated at 850°C for 30 minutes. These results indicate that the U_3Si_2 powder has fully reacted with the molten aluminum. Thus, along with no adjustment of the treatment cycle temperature these results indicate that reaction kinetics will also not limit the treatment cycle.

Figure 2. Ternary Isothermal Sections for the U-Al-Si Alloy System

Oxide Fuels and Metallurgical Treatment

Much like the silicide fuels the initial development of the uranium-oxide fuel stemmed from a desire to lower research and test reactor fuel assembly enrichment to produce non-proliferable fuels. Thus, the first assemblies produced containing U_3O_8-Al cores were either low enriched (20% ^{235}U) or medium enriched ([congruent] 45% ^{235}U). Later, however, highly enriched U_3O_8-Al cores were made and constitute the bulk of the oxide assemblies currently in service. Like the silicide fuels the uranium oxide fuel particles react with the aluminum matrix while in service as seen in Figure 4. However, the extent of the reaction in the oxide is much greater than in the silicide fuels. Efforts to document the phases present in the reaction zone have been inconclusive with only a few reports of UAl_x compounds and Al_2O_3 phases being reported.[6-8]

Figure 3. Post-Irradiation Microstructure for a U_3O_8-Al HEU Fuel (Adapted from Reference 6)

For the operation of the melt-dilute treatment process the composition of a typical oxide fuel assembly considering melting and full reaction of the oxide particles with the aluminum has been determined using a HIFIR core as representative. The final alloy composition for a fully molten and reacted HIFIR core is approximately 90-93 wt% aluminum, 6-10 wt% uranium and 1-2 wt% oxygen. In keeping with the binary UAl_x fuels, the expected final melt-dilute treatment process ingot composition will contain 13 wt% uranium. By keeping the uranium concentration the same for the two fuel types the final microstructures and performance properties will remain relatively similar.

The development of a treatment cycle for the oxide fuels within the bounds of an upper treatment cycle temperature of 1000°C is currently underway. The necessary treatment temperature for both the UAl_x and U-Al-Si fuels has been shown to be in the range of 800-850°C. For the sake of ease of process operation and off-gas, it would seem appropriate to attempt to operate the oxide fuel treatment cycle at similar temperature.

Recent experiments to develop an understanding of the kinetic behavior for the dissolution of U_3O_8 particle in molten aluminum has been performed. Specimens of depleted U_3O_8-Al fuel tube were heated for times from 1-4 hours in molten aluminum baths. A determination of the driving force for the dissolution reaction based on fundamental thermodynamics has shown that for the oxide fuels the expected reaction is as follows:

$$Al + U_3O_8 \rightarrow UAl_4 + Al_2O_3 + Al$$

This reaction should proceed as written for temperatures from 800-1000°C. Experimental data indicates that 75% of the oxide particles have reacted at 850-1100°C in 1-3 hours. Additions of calcium to the aluminum to form an Al-5wt% Ca alloy have been shown to enhance the reduction process. Oxide fuel tube sections can be fully reduced to produce metallic U-Al alloys using the Al-Ca solvent in less than 1 hour at 850°C.

"Ternary" Constituent Effects

Understanding the nature of ternary constituents in melt-dilute is fundamental to the development the treatment process and the off-gas system. Ternary constituents can potential impact processing temperatures, melt behavior, and of-gas system design and operation. The formation of deleterious compounds/secondary phases can potentially lead to increased processing temperatures, decreased Al-SNF form performance, and improper performance of the treatment process off-gas system.

Non-radioactive surrogates have been used to simulate their radioactive counterparts in bench-scale melting experiments. These melt experiments have been conducted with the anticipation of elucidating the impact these ternary radionuclide surrogate species may have on the release of cesium to the off-gas system and also to analyze the partitioning behavior of these species during solidification.

Surrogate samples were produced containing the following radionuclide surrogates: Cs, I, Se, Sr, Ce, Mo, Re, and Pd. These species where mixed with Al powder and pressed into a pellet that was placed in a U-Al (6061) alloy melt at 850°C. Following solidification of the melt, samples where sectioned from the ingot and metallographic and SEM analysis was performed. Preliminary SEM analysis of these samples indicates that the radionuclide surrogates Cs, Re, and Mo partition to the UAl_4 during solidification as shown in Figures 4. Further SEM analysis has shown that some of the alloying elements in the 6061 Al used in the melts also selectively partitioned. Silicon has been found to partition to the UAl_3 phase while iron partitions to the UAl_4 phase. The partitioning of these species is important because some of the MR type fuels to be treated with this process are clad in alloys that closely resemble 6061 or 5052 aluminum alloys.

Figure 4. SEM EDS Analysis Showing Cs, Mo, and Repartitioning to UAl_4

An off-gas system for the melt-dilute treatment technology is necessary due to the volatility of some of the "ternary" radionuclide/cladding alloy species. Some of the ternary species have significant vapor pressures (on the order of a few atmospheres) at the anticipated treatment operating temperature of 850°C. An examination of the vapor pressures of the radionuclide and cladding element inventory for a bounding MTR fuel indicates that the following species are of greatest concern with respect to volatilization: Cd, Cs, Mg, Te, Se, Kr, I_2, and Zn. Of these species the only two that are present in quantities greater than 1 gram are Cs and Mg. The ^{137}Cs isotope is greatest concern because it is a strong gamma emitter.

Melting of reactor fuel and core components causes release of volatile fission products from molten fuel. Fission products released from fuels have been studied extensively because of their importance to severe nuclear reactor accidents. These studies have analyzed the release of fission products from aluminum clad Al-U, Al-U_3O_8 and Al-U_3Si_2 fuels and have included both irradiated and unirradiated fuel plates as well as tests using simulated radioactive elements.[7,8,9] For Al-U fuels, investigators have reported cesium releases below 1000°C of 10 to 20%.[7]

Preliminary efforts to design an effective off-gas system have concentrated on the capture of ^{137}Cs. Bench-scale laboratory tests have been performed using non-radioactive Cs surrogates to evaluate off-gas system concepts. To date two absorber media, activated alumina and 4A zeolite, have been evaluated for their effectiveness at Cs capture. Bench-scale tests at SRS, under proposed melt-dilute process conditions, have indicated that the release of cesium is less than 5% as shown in Figure 5.[10]

Figure 5. Melt-Dilute Bench-Scale Off-Gas System Cesium Release Fractions

Additional tests have been conducted using small irradiated fuel coupons to provide further insight into the volatilization of "ternary" species. These tests have been performed in the Alpha-Gamma hot Cells at Argonne National Laboratory. For these tests a coupon of 45% ^{235}U enriched fuel that had a burn-up of approximately 80% was melted in a graphite crucible at 850°C and held for 1 hour at temperature. A small off-gas system was constructed that consisted of a zeolite absorber bed and a wet bubbler. Following the test gamma scans were performed on the test apparatus to determine if indeed any radioactive cesium had volatilized during melting and where it was located. Preliminary gamma scans of the test apparatus for Cs (Figure 6) show that the majority of the cesium in the fuel coupon remained in the crucible with the small fraction that did volatilize being trapped on the zeolite absorber bed.

Figure 6. Gamma Scan of Melt-Dilute Irradiated Fuel Coupon Test

Summary

The melt-dilute technology is a relatively simple and versatile process that can alleviate both nonproliferation and criticality concerns for the long-term storage of HEU spent nuclear fuel. An attribute of the melt-dilute process is its applicability to various types of FRR and DRR SNF. Data presented herein indicate that treatment of these different SNF types can be effected at temperatures below 1000°C. Binary U-Al Fuels can be treated at

these temperatures using either graphite or carbon steel crucibles with no impact on the process operation. Additionally, with the construction and validation of ternary isothermal phase diagram sections it has been shown that U-Al-Si fuels can be treated at temperatures below 1000°C. The treatment of the oxide fuels has also been proven viable in the temperature range of 1000°C and below with the addition of Ca as a reduction catalyst. The ternary constituents in the melt-dilute SNF form have been shown to partition to the aluminide intermetallic phases. This potentially could effect corrosion and release phenomenon and will be investigated further. Additionally, preliminary results from the ternary species volatilization experiments have indicated that while ^{137}Cs is of concern, it has been shown to be captured using a zeolite absorber bed. Thus, the melt-dilute treatment process for reducing HEU fuel to a LEU SNF form for geologic disposal is a quite versatile and completely viable treatment process.

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