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Zirconia-Based Materials for Transmutation of Americium and Curium : Cubic Stabilized ZrO_2 and Zr Oxide Pyrochlores

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Abstract

We present here experimental studies involving the incorporation of americium and curium elements in zirconia-based compounds, which are applicable for reactor transmutation schemes. Two materials are considered: Cubic-Stabilized Zirconia (CSZ) and the pyrochlore oxides having the formula, $An_2Zr_2O_7$, where An = Am, Cm.

Keywords: transmutation, americium, curium, zirconia, pyrochlore

1. Introduction

Independent of one's position on electro-nuclear energy, it is still environmentally the least- polluting method for producing electricity. There are no releases of "greenhouse-effect" gases or undesired acid pollutants. Some of the solid wastes of concern generated from this production method can be appropriately and safely handled by proper reprocessing and subsequent transmutation schemes. During fission processes, long-lived radioactive elements are generated, which included some actinides (neptunium, plutonium, americium, curium) and other long-lived fission products (^{99}Tc, ^{129}I, ^{135}Cs, etc.). One approach for disposal of these radioactive actinide elements, after they are partitioned, is to "burn" them in a dedicated nuclear reactor or a specific neutron source system. This process referred to as transmutation converts them via neutron interactions into materials with shorter a half-life, that are better suited for long term disposal. In this work, we focus on americium and curium elements.

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One scenario consists of recycling these elements in a uranium-free, host material. The goal is to stabilized those elements regarding against structural and thermochemical processes while avoiding the subsequent production of other actinide elements through neutron capture by uranium. The support matrix containing the target elements has to be selected carefully considering various criteria such as neutron cross section, chemical inertness (cladding, coolant, etc.), sufficiently high melting point, phase stability at elevated temperatures, thermal conductivity, etc. Several potential candidates have been envisioned and discussed previously. We discuss here some selected zirconia-based compounds.

2 Experimental

Materials:

The starting materials used for preparing the americium and curium zirconia based compounds were commercial high-purity (99.9%) Y_2O_3 and ZrO_2. The ^{243}Am and ^{248}Cm oxides used were of the same quality and made available by the U.S. Department of Energy through its heavy element research program at the Transuranium Research Laboratory at Oak Ridge National Laboratory (ORNL).

Sample Preparations:

Samples were prepared by different techniques, depending on the particular materials desired. For the americium oxide work, the starting materials were first calcined up to 1000°C to remove moisture, volatile material, carbonates, etc. Weighed portions of these products were then mixed/ground thoroughly and then calcined at temperatures up to 1500°C for some 20 hours with intermittent grindings. For the Cm samples, given the scarcity of the special isotope, the preparations started by taking appropriate alloquets of aqueous nitrate solutions of the components, slowly drying these solutions to dryness and then calcining these solids to the desired temperatures. All the preparations were done with sub-gram quantities of material.

X-ray Analysis

All sample materials were characterized by X-ray diffraction using 114.6 mm Debye-Sherrer analysis in conjunction with molybdenum K_α radiation ($\lambda_{avg.}$ = 0.71073 Å). The radioactive samples were sealed in quartz capillaries for the analyses. The cell parameters were refined from the observed reflections using a least square method (LAPOD program).

3. Americium and curium transmutation : important aspects to be considered.

Americium 241 and curium 244 are the primary isotopes likely to be encountered during irradiation of uranium/plutonium materials. The ^{241}Am ($t_{1/2}$ = 433 yr) isotope decays by alpha emission to ^{237}Np. The highest oxide of americium, AmO_2, exhibits a fluorite type structure : a = 0.5386 nm [1]. Americium is frequently considered the first actinide to exhibit lanthanide-like properties, especially in its trivalent state, although actinides appearing earlier in the series may also be included in certain oxidation states and specific situations (e.g., Pu_2O_3 solid-state behavior).

As a result of the changing stability of electronic configurations along the actinide series, AmO_2 is less thermally stable than PuO_2, and it begins to loose oxygen at temperature as low as 900°C. The sesquioxide

of americium appears as the probable oxide at higher temperatures (>1200°C) [2,3]. The oxygen potential over AmO_2 becomes significant and as a result there are some concerns about potential corrosion of the cladding elements. In addition to this corrosion, according to the calculated Am_2O_3-AmO_2 phase diagram [4], a diphasic material can be encountered for oxygen/metal ratios less than 2, and this could lead to potential swelling of targets. Both a body-centered-cubic and a hexagonal form of the sesquioxide have been established.

Another important aspect for americium is the thermal conductivity of AmO_2, which is low (0.69 W/mK [5]) and decreases about 30% in a short period (50 days) due to self-radiation damages from α-decay [4]. The later can promote the thermal reduction of AmO_2 and there exits some potential for vaporization of elemental Am from targets via decomposition of oxides, given the low energy of decomposition of AmO and the high volatility of Am metal [6]. The loss of americium from different materials at elevated temperatures has been discussed in general [7].

The ^{244}Cm ($t_{1/2}$ = 18.1 y) isotope decays by alpha emission to ^{240}Pu ($t_{1/2}$ = 6564 y). Curium is usually encountered in a trivalent state compounds but a dioxide with fluorite structure is formed in an oxidizing atmosphere at ~400°C [8]. However, an O/M ratio of two is difficult to and stabilize, and above 400°C CmO_2 is reduced eventually to form a sesquioxide. As found with lanthanide sesquioixdes, actinide sesquioxides are also multiphasic, and Cm_2O_3 exhibits two phase transitions (to monoclinic and then hexagonal) between room temperature and its melting point (2260 ± 25 °C) [9].

Americium and curium are difficult to separate during fuel reprocessing due to their similar chemical properties in aqueous media. Thus, the concept in this paper is to "burn" both americium and curium in the same transmutation scheme, which is an important aspect to consider from the perspective of industrial and radiotoxicity benefits [10].

4. Cubic stabilized Zirconia and Pyrochlore oxides

We recently determined that a 25 mol% yttria-cubic stabilized zirconia (YCSZ) is a suitable material for a diluent host material for the transmutation of actinides[11]. It is a stable refractory ceramic having a fluorite-type structure, which remains single-phased up to its melting point (2600°C). This material exhibits high chemical and physical stability and has also a good radiation and fission product resistance [12]. We have shown that YCSZ can incorporate significant quantities of americium dioxide in its fluorite type matrix (up to 6.5 g/cm^3). The cell parameters of these products were found to be linear with the AmO_2 composition.

When initially considered, zirconia appeared less attractive than other materials, due to its low thermal conductivity (~2W/mK). However, given the proposal that actinide-containing targets could be irradiated at low power for several years (which would generate a lower heat flux), zirconia has again been considered. One interesting scheme for overcoming the poor thermal conductivity of zirconia is to use a diphasic material. This concept, developed by different authors [13,14], is based on the dispersion of zirconia beads in an insoluble inert material that has a higher thermal conductivity. An example cited in reference [13], where the authors studied the thermal-physical properties of the spinel, yttria stabilized zirconia system up to 1800 K. It was shown that for a material composed of 22.5 % in volume of Y-CSZ

dispersed in a $MgAl_2O_4$ matrix, the effective thermal conductivity of the composite material is about 30 percent higher than uranium dioxide.

We have recently studied the behavior of Am-YCSZ materials under reducing atmospheres and concluded that above 30 mol % AmO_2, thermal reduction of the actinide oxide could lead to a diphasic system. Thus, such loading in Y-CSZ is not desirable.

However, if larger concentrations of Am are needed in a matrix, we propose the use of another zirconia-based material. This material, which belong to the family of pyrochlore oxides, has the formula, $An_2Zr_2O_7$ (where An = Am, Cm). Indeed, pyrochlore oxides as well as Y-SCZ are suitable and offer a potential as reactor transmutation matrices for actinides. In comparison, a Y-CSZ matrix offers a 30 mol % content of Am, while the content is about 62 % in $Am_2Zr_2O_7$.

The pyrochlore zirconia oxide ($A_2Zr_2O_7$) is also refractory ceramics and remains single phased up to its melting point (>2000°C). The material also has a fluorite type structure with a double unit cell, which has an ordered deficiency of oxygen atoms. In such pyrochlores, the actinide is a trivalent cation, eight-fold coordinated and the Zr is tetravalent and sixfold coordinated. Both cations have long range order. This pyrochlore oxide can be visualized as being a reduced form of a cubic $(An_{0.5}Zr_{0.5})O_2$ solid solution, where the actinide cation has been reduced.

One advantage of the americium material is the low oxygen potential that can be expected, given the trivalent oxidation state of americium (comparable with the Am_2O_3 oxygen potential [4]). For this material, corrosion of the cladding is of less concern. There is no need then for stabilizing agents in these compounds. Finally, we demonstrated in previous studies that several actinides can form such zirconia based pyrochlore oxides [15,16].

5. Conclusion

The concept of using a composite of material for transmutation of americium and curium offers two main advantages. One is to provide a suitable thermal conductivity for high temperature applications. The second is to retain fission products localized in the host material, and keep the bulk material free of fission product damages. Depending of the desired loading for americium and curium, either Y-CSZ or pyrochlore oxides of the type, $An_2Zr_2O_7$, can be employed and this offers versatility in selecting a host matrix for transmutation.

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