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Letter to the Editor

Comments on americium volatilization during fuel fabrication for fast reactors

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ABSTRACT

The physical processes relevant to the fabrication of metallic nuclear fuels are analyzed, with attention to recycling of fuels containing U, Pu, and minor volatile actinides for use in fast reactors. This analysis is relevant to the development of a process model that can be used for the numerical simulation and prediction of the spatial distribution of composition in the fuel, an important factor in fuel performance.

1. Introduction

Transmutation of long-lived radionuclides is a potential technology for the treatment of spent fuel from nuclear reactors [1]. Minor actinide (MA) metals exhibit large vapor pressures, e.g., 0.1 kPa at 1500 K for Am [1] and their containment is one main challenge for the fabrication of transmutation fuels. Moreover, the transmutation fuel must be fabricated while maintaining adequate thermal conductivity, chemical stability, melting point, uniform distribution of MA, and ability to sustain radiation damage. The fabrication must be simple and compatible with remote manipulation and automation. Traditional fabrication processes for nuclear fuel cannot meet all the requirements for the fuels containing MA and new processes must be designed [1,2]. The transition from current materials and process designs to those for fuels containing MA will greatly benefit from computational analyses that can predict the distribution of MA in fuel, material properties within the component, and ensuing fuel performance. This paper addresses the development of a model for predicting the Am volatilization for the numerical simulation of the fabrication process.

2. Constitutive equations

Due to the high partial pressure of Am over the alloy, an inert gas atmosphere is very likely to be used. The amount of Am volatilization depends on the rate of evaporation at the material surfaces, transport by diffusion in the bulk of material (liquid and/or solid), and mass transfer within the gas/vapor region. The ideal rate of vaporization into a vacuum is given by Langmuir's equation. The net evaporated flux is the difference between the evaporated and condensed fluxes. For a single component system, the relationships for the volatilization flux shown in Table 1 were derived using the non-linear moment solutions to the Boltzmann equation within the Knudsen layer that can be used in conjunction with macroscopic continuum fluid dynamics in the gas domains [3].

In the presence of an inert gas atmosphere, the vaporization rate is limited by the diffusion of molecules from the near-surface boundary layer [4], and the vaporization flux depends on the distance from the vaporization surface to the sink, where the concentration becomes equal to that in the bulk [4]. The vaporization-to-sink distance is an empirical lengthscale and was shown to be one of the significant sources of errors. For the evaporation of liquid droplets in combustion systems, empirical correlations are given [5]. Thus, the contribution of gas flow and gas molecules to the general kinetic theory for evaporation within the Knudsen layer has yet to be considered on a more formal basis.

The mass flux from the dense phase to the vapor phase can be described, using the concept of a mass transfer coefficient (MTC) [6], as the product between the MTC and concentration difference (Table 1). The residence time depends on the transversal velocity and length scale of the free surface [6]. The concentration difference of species *i* can be that across the gas phase boundary layer, $C_{g,L} - C_g$, or liquid phase boundary layer, $C_L - C_{L,g}$.As the interface concentration, $C_{g,L}$ and $C_{L,g}$, are not directly available, it would be more convinent to write the formulations based on the bulk concentration of gas (liquid) phase which would be in equilibrium with that in bulk liquid (gas) $C_{*,g}(C_{L,*})$ [7]. Due to the asymmetry in the evaporation equations [3], the set of equations given in Table 1 cannot be combined into simpler formulations based on series resistance models like those in [6].

3. Microstructure effects on Am distribution

The type of microstructure determines the distribution of Am in the fuel. In order to limit Am vaporization, rapid thermal processing can be used to hold the time in the melt and/or higher temperatures to a minimum. It is expected that due to high cooling rates in the metallic fuel, both columnar and equiaxed microstructure will be formed. During solidification, Am is rejected to the liquid. Thus, a lower concentration of Am is expected in the columnar

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Nomenclature

A	evaporation area (m^2)
C	concentration $C_{L,g} = \bar{\rho}_M N_i$ (mol/m^3)
$C_{*,g}$	bulk concentrations of gas phase which would be in equilibrium with that in bulk liquid
$C_{L,*}$	bulk concentrations of liquid phase which would be in equilibrium with that in bulk gas
D	diffusion coefficient (m^2/s)
Hv	heat of vaporization (J/mol)
j	molar flux ($mol/m^2\,s$)
k	mass transfer coefficient (m/s)
M	molar mass (kg/mol)
$\bar{M}$	alloy molar mass (kg/mol)
m_L	slope of the gas phase concentration in equilibrium to the liquid phase concentration
N	mol fraction in the liquid
P_s	vapor pressure of pure element, Pa,
R	ideal gas constant (J/(mol K))
T	temperature (K)
V	alloy volume (m^3)
β and F^-	coefficients [3]
γ_i	chemical activity coefficient of element
$\bar{\rho}$	alloy density (Kg/m^3)
$\bar{\rho}_M = \frac{\bar{\rho}}{\bar{M}}$	alloy molar density (mol/m^3)
τ_r	residence time of liquid on surface, s (τ – integration variable)

Subscripts

c	condensation
e	evaporation
g	gas
g, L	interface gas–liquid on the gas side
i	specie
io	initial
L	liquid
L,g	interface liquid–gas on the liquid side
M	alloy
o	reference state
s	surface for temperature

Table 1
Equations for the mass fluxes at the fuel surface

Medium/ phenomena	Flux	MTC	Overall flux
Metal	$j_{A,L} = k_{M,L}(C_L - C_{L,g})$	$k_{M,L} = 2\sqrt{D/(\pi\tau_r)}$	–
Gas	$j_{A,g} = k_{M,g}(C_{g,L} - C_g)$		$j_{A,g} = k_g(C_{*,g} - C_g)$
Evaporation	$j_{A,e} = k_{M,e}C_{L,g} - k_{M,c}C_g$	$k_{M,e} = \dfrac{\gamma_i P_s}{\bar{\rho}_M\sqrt{2\pi M_i R T_s}}$, $k_{M,c} = \dfrac{\beta F^- P_g}{\bar{\rho}_M\sqrt{2\pi M_i R T_g}}$	–

$P_s(T_s) = P_o \exp[-(1/T_s - 1/T_o)H_v/R]-$ –Clausius–Clapeyron equation.
$1/k_g = 1/k_{M,g} + m_L/k_{M,L}$ – overall MTC for the gas side, $m_L = (C_{g,L} - C_{*,g})/(C_{L,g} - C_L)$.

region of the fuel than in the equiaxed region [8]. Also, the ensuing distribution of Am will be more uniform in equiaxed regions than in those of columnar microstructure. Porosity may alter the fuel quality. A centerline porosity can result when the center of the fuel rod is the last region to solidify. In regions where severe shrinkage is experienced, the pressure can reach the cavitation limit and microporosity can be high and its morphology is irregular and interdendritic [9]. Am and other volatile elements can affect porosity formation in metallic fuels since the nucleation and growth of pores in solidifying alloys has been shown to be influenced by the partial vapor pressure of volatile solute elements [9,10].

4. Wetting behavior at the interface between the fuel-container

In order to hinder chemical reactions between the mold and metal, a non-wetting behavior between the liquid metal and mold is desirable. When the mold surface is hydrophobic, the liquid surface is not in continuous contact with the mold surface, exhibiting gas areas that are connected along the surface (Fig. 1). Thus, the non-wetting behavior can yield an increase in the vaporization area, which can be detrimental to the Am containment. The effect of the hydrophobic nature of surfaces was studied for permeable media [11,12]. Recently, molecular dynamics simulations were used to study the phenomena encountered at hydrophobic surfaces [13,14], such as the effect of gas accumulation in narrow wall confinements.

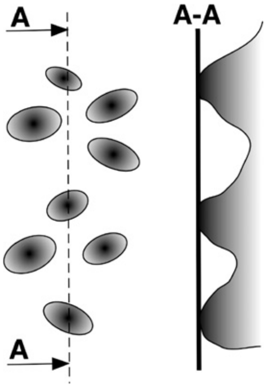

Fig. 1. Schematic of contact for a hydrophobic surface. Black and gray areas indicate contact between the liquid and the mold. White indicates vapor/gas regions.

5. Results for Am volatilization for hydrophobic and hydrophilic container surface

Results are presented in this section for the 40Zr–10Am–10Np–40Pu fuel (wt%) [15]. For this alloy, $\bar{\rho} = 10\,000$ kg/m^3 and $\bar{M} = 0.1458$ kg/mol. Since both the material data and a comprehensive computational model are not available, results are presented in this section only for the Am evaporation, i.e., $\gamma_i = 1$ and $M_i = 0.243$ kg/mol. For an uniform concentration distribution, the instantaneous change in the atom fraction of Am, due to the evaporation in a time interval, dt, is given as [16]

$$\frac{dN_i}{N_i} = -k_{M,e}\frac{A}{V}\,dt. \tag{1}$$

The Am loss fraction is given as

$$(N_{io} - N_i)/N_{io} = 1.0 - \exp\left(-\int_0^t \frac{k_{M,e}(T(\tau))}{V/A}\,d\tau\right). \tag{2}$$

For a typical pellet of diameter and height 1 cm, the V/A was 1 and 0.2 cm for the wetting (W) and hydrophobic (NW) cases, respectively, i.e., when the vaporization was considered to take place only through the top surface and through the top surface and side surface of the mold, respectively. It was considered that the temperature in the pellet was constant. For Am, the data from [17] was

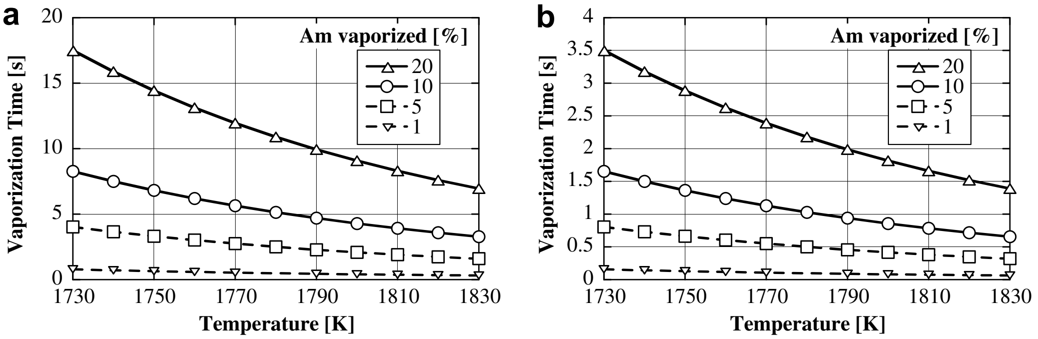

Fig. 2. The residence time as a function of holding temperature (a) wetting and (b) non-wetting cases.

used to yield $Hv = 0.255544$ MJ/mol, $T_0 = 1650$ K, and $P_0 = 557.44$ Pa. The exact melting temperature was not available for this particular alloy. For 67.9U20Pu10Zr2.1Am (wt%), the melting temperature was 1588 K, while the casting temperature recommended was 1738 K [18]. The time to reach a certain percentage loss of alloy content is referred to as the vaporization time. The vaporization time varies from several fractions of second to several seconds to reach losses from 1% to 20% (Fig. 2). The result indicated that for the non-wetting case, the vaporization time is approximately one fifth that for the wetting case, indicating that the wetting behavior is an important factor that needs to be considered in more detailed models. This data is qualitative and more accurate results could be attained with more comprehensive models that would account for the non-uniform distribution of the temperature and concentrations within the fuel.

6. Conclusions

The fuel fabrication must include a detailed system analysis since all the time intervals for heating, melting, holding, and/or solidification need to be minimized in order to retain Am in the fuel. Microstructural effects need to be considered for predicting Am distribution. Constitutive equations for mass transport of volatile species in the presence of an inert gas atmosphere include liquid- and gas-phase diffusion. It was found that the wetting properties between the fuel and mold have an important effect on Am loss. The data on times for vaporization of a specific percentage of Am can be used to design and evaluate rapid thermal processes for fuel fabrication.

The data on the spatial distribution of composition of U, Pu, and actinide compounds is important to the further evaluation of fuel performance. This work is a prerequisite for developing computational tools that will be used to reveal key microstructure features, porosity size and distribution, actinide spatial distribution, and possible defects in the fuel components due to processing conditions.

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