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Kinetics of and Atmospheric Effects on Gallium Removal from a CeO_2 Based Mixed Oxide Surrogate

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ABSTRACT

This paper describes preliminary experimental results on the kinetics of Ga removal from Ga_2O_3 -doped CeO_{2-x} , a surrogate for weapons grade PuO_{2-x} . Ga is removed from the surrogate feedstock material using thermal techniques. An Ar-6% H_2 gas was used in order to reduce the oxide to gaseous Ga_2O . Experiments were done in the temperature range of 600-1200°C as a function of time, gas flow rate, and sample geometry. Samples were analyzed through measurements of weight change, scanning electron microscopy/energy dispersive spectroscopy, x-ray photoelectron spectroscopy, proton induced x-ray emission, and direct current plasma analysis. Gallium levels were reduced by as much as 98% (130 ppm Ga residue) of that in the starting material. Studies to date have shown CeO_{2-x} is a very good surrogate for PuO_{2-x} .

BACKGROUND

Currently there is interest in fissioning weapons grade plutonium in nuclear reactors, making use of its valuable energy while at the same time reducing certain dangers associated with its potential for nuclear weapons proliferation.^{1,2} In the process of dismantling and declassifying nuclear weapons, the U.S. intends to convert much of the Pu metal to oxide using a hydride-dehydride process. This process yields a PuO_{2-x} powder which potentially can be incorporated into a mixed oxide nuclear fuel (MOX), a mixture of PuO_2 and UO_2 , or potentially in an advanced non-fertile fuel. However, unlike reactor grade Pu, weapons grade Pu contains minor additions of gallium in order to stabilize the δ -phase and improve the machinability of the alloy. Gallium (melting point = 30°C) is a known embrittling agent and alloys rapidly with most metals.³⁻⁷ Consequently, to assure proper cladding and fuel performance, Ga must be largely removed from weapons grade plutonium before it can be processed and used.

In order to avoid aqueous processing of this material, which produces considerable additional waste, we have proceeded toward the development of a relatively simple thermal process for removing gallium from PuO_{2-x} with the objective of achieving parts-per-million levels. Our proposed removal process involves heating the oxide in an Ar- H_2 environment, probably at temperatures in excess of 1000°C, producing as the primary gaseous product $\text{Ga}_2\text{O}(\text{g})$ from decomposition of the Ga_2O_3 present in the mixture. As described later, the equilibrium partial pressure of $\text{Ga}_2\text{O}(\text{g})$ above Ga_2O_3 is relatively high in a reducing atmosphere. Once evolved, the $\text{Ga}_2\text{O}(\text{g})$ is swept away from the PuO_{2-x} by the gas

stream and must be collected and removed from the heat treatment system. In this paper, we briefly communicate some of the important fundamentals of the thermodynamics and kinetics of the processes of vaporization and deposition using CeO_{2-x} as a surrogate for PuO_{2-x} . Due to similarities in thermodynamic properties, d-orbital bonding, Ga solubility, oxygen diffusivity, and nonstoichiometry, CeO_{2-x} has been proposed as a reasonably good surrogate for PuO_{2-x} .³⁻¹⁵ In addition, a well characterized surrogate outside of a glove box environment aids evaluations for pilot or full scale production equipment, thus preventing unnecessary radiation exposure to personnel, excessive levels of radioactive waste, and costly errors that could be associated with setting up a large scale system in a glove box without the advantage of a prior operational checks.

Figure 1. Green and fired densities of CeO_2 -2wt.% Ga_2O_3 pellets after the steps described in the experimental procedure. Note, "n" represents the number of specimens on which measurements were made, "a" denotes average percent theoretical density, and "s" denotes standard deviation.

EXPERIMENTAL PROCEDURES

CeO_2 -based MOX surrogate feedstock material was prepared by blending, sintering, and milling CeO_2 plus 2 wt% Ga_2O_3 powders. The overall process were summarized as follows; The desired quantities of CeO_2 and Ga_2O_3 powder were measured and blended, and vibration milled in a small SPEX mill for 20 minutes. The powder was pressed into 1/4" x 1/8" diameter pellets to $\approx 35\%$ of theoretical density in the green state. The green pellets were milled again and sifted through a -150 μm screen and then pressed into 1.1 cm x 0.65 cm diameter, $\approx 65\%$ dense pellets. The pellets were then fired at 450°C for 4 h to remove the binder and were immediately sintered at 1650°C for 4 h in air. After sintering, the pellet density was measured by the Archimedes method. The sintered pellet was then re-crushed to desired particle size distributions. The densities of pellets are shown as a function of processing step in Fig. 1. Figure 2 shows the measured Ga content of the surrogate before and after sintering compared with a nominally 1 wt% Ga_2O_3 - PuO_2 material calculated. From this figure, it is apparent that Ga loss during sintering provided a surrogate with a Ga content comparable to that in weapons grade PuO_2 feedstock material.

Gallium removal studies were performed by exposing different powder lot sizes of the surrogate feedstock as well as complete pellets to ultra-high purity Ar-6% H₂. In this paper we report the results of experiments performed in the temperature range of 600-1200°C as a function of time, gas flow rate, particle size, and sample size or geometry. The samples consisted of 0.3, 0.9, and 2.5 gram lots, as well as pellets, which rested in small alumina boats. The boats were placed in the hot zone of a controlled atmosphere alumina tube furnace. The oxygen partial pressure was controlled at $\approx 10^{-21}$ ppm during the thermal treatments. Surrogate powder and pellet samples were heated to the desired temperature at 20°C/min and held between 0.5 to 12 hours. The weight change of surrogate was monitored before and after exposure (although some weight gain did occur upon re-exposure to air due to O₂ pick up by substoichiometric CeO_{2-x}). Samples were analyzed by scanning electron microscopy/energy dispersive analysis (SEM/EDS), x-ray photon electron spectroscopy (XPS), Rutherford backscattering spectrometry (RBS), proton induced x-ray emission (PIXE), direct current plasma emission spectroscopy (DCP), and Leco TC-136 oxygen/nitrogen analysis.

Figure 2. Measured Ga concentration in the ceria based surrogate powders before and after sintering compared with that in a nominal 1 wt% Ga₂O₃-PuO₂ mixture.

RESULTS AND DISCUSSION

Thermodynamic data for the Ga-O-H system were collected¹⁶ and free energies of formation were fit, using stepwise multiple linear regression, to the equation:

$$\Delta G_f = a + bT + cT^{-1} + dT^2 + eT^3 + fT \ln T \quad (1)$$

where $a-f$ are constants, and T is the temperature in degrees Kelvin. Table 1 shows some of the data pertinent to this brief analysis. Note that other gaseous products such as Ga, GaH, GaO, Ga₂O₂, and Ga₂O₃ are not included in these analyses because their equilibrium partial pressures are comparatively low. The constants in Table 1 were used to calculate temperature dependent expressions for

the vaporization behavior of gallium oxide from doped PuO_2 in Ar-6% H_2 . A temperature dependent expression for the free energy of reaction can be determined from the mass action equation:

From this equation the following relationship was derived from which $\text{Ga}_2\text{O}(\text{g})$ partial pressures can be calculated:

$$p_{\text{Ga}_2\text{O}} = \frac{a_{\text{Ga}_2\text{O}_3} p_{\text{H}_2}^2}{p_{\text{H}_2\text{O}}^2} \exp \left[91.3647 + 1.1203 \cdot 10^{-3} T - 7.761944 \cdot 10^{-8} T^2 - \frac{64223}{T} + \frac{157638}{T^2} - 7.8179 \ln T \right] \quad (3)$$

Where a and p represent activity and equilibrium partial pressure, respectively.

Alternatively, the vaporization of $\text{Ga}_2\text{O}(\text{g})$ may be assessed using the mass action equation:

where the partial pressure of $\text{Ga}_2\text{O}(\text{g})$ may be calculated using the equation:

$$p_{\text{Ga}_2\text{O}} = \frac{a_{\text{Ga}_2\text{O}_3}}{p_{\text{O}_2}} \exp \left[75.69396 - 3.7071 \cdot 10^{-4} T + 2.50277 \cdot 10^{-8} T^2 - \frac{121066}{T} + \frac{117327}{T^2} - 3.82324 \ln T \right] \quad (5)$$

Equation (5) may be substituted for equation (3) by considering how the partial pressure of oxygen is controlled by the $\text{H}_2/\text{H}_2\text{O}$ ratio according to buffer reaction:

It is apparent from equations (5) and (6) that the higher the $\text{H}_2/\text{H}_2\text{O}$ ratio, the higher will be $p_{\text{Ga}_2\text{O}}$ (i.e., $p_{\text{Ga}_2\text{O}}$ is inversely related to p_{O_2}). Thus, the vaporization of Ga_2O would be expected to be more rapid in dry versus moist hydrogen. The equations described above can be used to calculate the equilibrium partial pressures of Ga_2O above various PuO_2 - Ga_2O_3 solid solutions. In a typical PuO_2 feedstock, it is anticipated that $a_{\text{Ga}_2\text{O}_3}$ will be on the order of 0.01 prior to any efforts to remove Ga. However, at this date, the activity of Ga_2O_3 in a typical PuO_2 feedstock powder is not precisely known; therefore, for the purpose of illustration

we must assume certain values of $a_{\text{Ga}_2\text{O}_3}$. Figure 3, shows how the vaporization behavior varies with environment as a function of $a_{\text{Ga}_2\text{O}_3}$. The calculations were done assuming the gas was a dry mixture of 1 atm of 6% H_2 and a balance of inert gas, such as Ar or He. This gas composition represents the experimental gases we are using in our Ga removal studies. It is apparent from Fig. 3, that the vaporization rate under the reducing effect of H_2 is relatively high, for example at 1000°C (1273 K) $p_{\text{Ga}_2\text{O}}$ varies between 10^{-4} and 10^{-2} for $a_{\text{Ga}_2\text{O}_3}$ between $1 \cdot 10^{-6}$ and 1, respectively. Thus, in a dry hydrogen environment, at elevated temperatures, Ga_2O_3 will vaporize relatively rapidly according to equation (2).

Table 1. Summary of constants shown in equation 1.

Compound	a	b	c	d	e	f
Ga_2O_3 (s)	-1123572.	574.0020	2267569.	5.3080E-03	-6.8814E-07	-31.7864
Ga_2O (g)	-117031.	-55.3176	1295110.	8.3901E-03	-8.9622E-07	0
H_2O (g)	-236296.	-65.1431	-169071.	-6.2395E-03	4.2670E-07	16.6059

Figure 3. Calculated thermodynamic equilibrium of $\text{Ga}_2\text{O}(\text{g})$ above $\text{Ga}_2\text{O}_3(\text{s})$ in 0.06 atm of H_2 as a function of temperature and $a_{\text{Ga}_2\text{O}_3}$.

The results of studies of the kinetics of Ga removal are presented in Figs. 4 and 5. Figure 4 shows the measured weight change observed as a function of temperature for the surrogate pellets and the three powder lot sizes. The weight changes measured in Ar-6% H_2 are contrasted to weight changes measured in pure Ar. It is noteworthy that following treatments in Ar-6% H_2 the powder appeared grey and metallic, while powder treated in pure Ar remained yellow-white. The data in Fig. 4 demonstrates that the surrogate is reduced in Ar-6% H_2 , but is not significantly reduced in pure Ar, which is in agreement with the thermodynamic calculations described above. However, the weight loss observed in Ar-6% H_2 is due to a combination of Ga loss and reduction of CeO_{2-x} to a more

substoichiometric compound.^{17,18} The data presented in Fig. 5, which shows measured Ga concentrations, are required to fully elucidate the kinetics of Ga removal. The data in this figure clearly show that there is a strong correlation between total weight loss and Ga loss. Chemical analyses of samples heat treated in pure Ar showed no significant loss of Ga. This data serves to illustrate that a significant fraction of Ga can be thermally removed via the reaction between H_2 and the oxide as described above. There is clearly a strong correlation between Ga loss and temperature. It appears temperatures in excess of $1000^\circ C$ will be required to achieve reasonable low levels of Ga.

Figure 4. Plot of weight change versus temperature for CeO_2 -2wt.% Ga_2O_3 surrogates exposed to Ar-6% H_2 and Ar for 30 minutes.

Figure 5. Plot of residual Ga versus temperature for 2.5 gram lots of CeO_2 -2wt.% Ga_2O_3 powder exposed to Ar-6% H_2 for 30 minutes.

As illustrated in Fig. 6, the Ga level can be reduced further through longer heat treatments, although the kinetics are nonlinear. As shown in Fig. 6, levels as

low as 130 ppm Ga have been achieved. As shown in Fig. 7, there did not appear to be a significant effect of particle size on Ga loss, despite a fair amount of scatter in the data. It is anticipated that Ga transport through PuO_{2-x} is at least as rapid as through CeO_{2-x} .

Figure 6. Plot of residual Ga versus time for CeO_2 -2wt.% Ga_2O_3 sample exposed to Ar-6% H_2 at 1200°C.

Figure 7. Particle size effect on residual Ga as a function of temperature for CeO_2 -2wt.% Ga_2O_3 surrogate exposed to Ar-6% H_2 for 0.5 h at 1.5 cm/sec flow rate.

Studies of lot size have shown that lot size does affect the rate of Ga removal, as shown, for example in Figs. 8 and 9. However, studies of the effects of gas flow rate (between 1.5 and 6.0 cm/sec true velocity) have shown no effect on Ga removal. The combination of these experiments lead us to propose that the rate of reaction is rate limited by transport of $\text{Ga}_2\text{O}(\text{g})$. Additional experiments are going on for the interpretation. A more extensive publication of these results as well as supporting kinetic modeling will be reported in a future publication.

Gallium deposition (following vaporization) is also an important issue in the design of a Ga removal system. We have conducted a number of studies of the Ga deposition products on the furnace wall, as summarized by the XPS results in Fig. 10. As discussed above, Ga_2O_3 vaporizes in H_2 to $\text{Ga}_2\text{O}(\text{g})$ at elevated temperatures. During thermal processing the $\text{Ga}_2\text{O}(\text{g})$ moves to cooler zones of the furnace, back reacts with $\text{H}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ and condenses out as $\text{Ga}(\text{l})$ and $\text{Ga}_2\text{O}_3(\text{s})$. Upon removal from the furnace, the exposed Ga rapidly forms a surface oxide of Ga_2O_3 . In agreement with these thermodynamic predictions, the XPS data of Fig. 10 demonstrate that the deposition product contains Ga_2O_3 and metallic Ga. Analysis of the XPS spectra also revealed an intermediate oxidation state for Ga. The precise bonding of this state could not be demonstrated conclusively. Although it is suggested that it may be solid Ga_2O from gas phase deposition, such a suboxide bonding configuration could be due to grading of the atmospherically produced oxide layer.

Figure 8. Relative Ga concentration as a function of lot size, measured by PIXE. Samples were exposed to Ar-6% H_2 at 1200°C for 30 minutes.

CONCLUSIONS

Studies of gallium loss were performed using CeO_2 surrogate for PuO_2 system as a function of atmosphere, particle size, sample lot size (configuration), and gas flow rate. It is shown that Ga can be removed thermally in an Ar-6% H_2 environment by the reduction of the oxide to $\text{Ga}_2\text{O}(\text{g})$, which is subsequently transported away from the solid. Studies have shown that Ga loss depends on sample lot size, exposure time, and temperature but not significantly on flow rate or particle size. Further studies are underway to correlate between results of the kinetics modeling to experimental data and pilot system.

Figure 9. Relative Ga concentration as a function of lot size, measured by XPS. Samples were exposed to Ar-6% H₂ at 1200°C for 30 minutes.

Figure 10. Simulation compared with the measured Ga LMM spectrum from the deposit on the furnace wall (minutes of air exposure following removal from the heat treatment furnace). In addition to the Ga₂O₃ and metallic Ga components used in the simulation, a third contribution (GaO_x) has been introduced that indicates the existence of an intermediate Ga oxidation state (or states). The difference spectrum compares the data with the simulation.

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