

# Helium interactions with alumina formed by atomic layer deposition show potential for mitigating problems with excess helium in spent nuclear fuel

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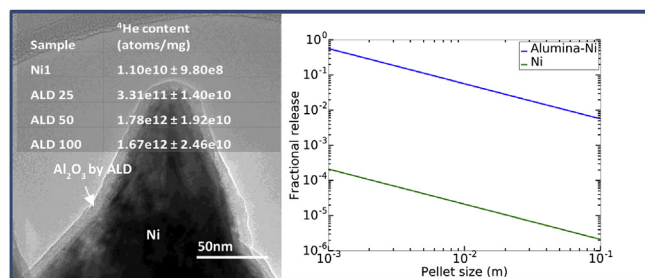
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## GRAPHICAL ABSTRACT



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## ABSTRACT

Helium gas accumulation from alpha decay during extended storage of spent fuel has potential to compromise the structural integrity of the fuel. Here we report results obtained with surrogate nickel particles which suggest that alumina formed by atomic layer deposition can serve as a low volume-fraction, uniformly-distributed phase for retention of helium generated in fuel particles such as uranium oxide. Thin alumina layers may also form transport paths for helium in the fuel rod, which would otherwise be impermeable. Micron-scale nickel particles, representative of uranium oxide particles in their low helium solubility and compatibility with the alumina synthesis process, were homogeneously coated with alumina approximately 3–20 nm by particle atomic layer deposition (ALD) using a fluidized bed reactor. Particles were then loaded with helium at 800 °C in a tube furnace. Subsequent helium spectroscopy measurements showed that the alumina phase, or more likely a related nickel/alumina interface structure, retains helium at a density of at least 10<sup>17</sup> atoms/cm<sup>3</sup>. High resolution transmission electron microscopy revealed that the thermal treatment increased the alumina thickness and generated additional porosity. Results from Monte Carlo simulations on amorphous alumina predict the helium retention concentration at room temperature could reach 10<sup>21</sup> atoms/cm<sup>3</sup> at 400 MPa, a pressure predicted by others to be developed in uranium oxide without an alumina secondary phase. This concentration is sufficient to eliminate bubble formation in the nuclear fuel for long-term storage scenarios, for example. Measurements by others of the diffusion coefficient in polycrystalline alumina indicate values

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several orders of magnitude higher than in uranium oxide, which then can also allow for helium transport out of the spent fuel.

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## 1. Introduction

Nuclear reactor fuels are typically dense uranium oxide formed into ~ cm scale pellets and encapsulated in metal for isolation from reactor coolant. Decaying actinides, e.g. short-lived actinides that are produced by capture reactions, as well as  $n, \alpha$  and  $n, n + \alpha$  reactions, lead to emission of alpha particles. The volumetric generation of helium from these alpha particles is then a significant concern during long-term spent fuel storage. Actinides actively produce helium during spent fuel storage, such that the increasing helium concentration can plausibly reach its low solubility limit in uranium oxide [1] after more than a hundred years in a repository [2,3]. Due to helium's low diffusion rate below 400 °C [3] under typical repository conditions, helium build-up in grains or at grain boundaries introduces potential for both pellet cracking and fuel embrittlement [3–8]. Although the specific outcome of helium accumulation on the microstructure evolution of reactor fuel is still under study, alleviation of helium buildup can be generally useful for a wide range of spent fuel storage scenarios.

In time, helium migrates along crystallographic grain boundaries over transport distances measured in microns [2]. If the gas could be sequestered in void spaces provided at the time of fuel preparation, or if an alternative diffusion path could be introduced for helium to escape the fuel rod to a controlled collection volume, then in principle the end-of-life pressure could be kept low enough to prevent distortion of the fuel. Previous investigations have focused on improving diffusivity of fission gases in nuclear fuel materials, mainly by doping additives into the uranium oxide matrix [9,10]. In particular, work done by Turnbull and Friskney [11] demonstrated that optimizing diffusion mechanisms along grain boundaries was useful to eliminate gas buildup.

However, there may also be utility in incorporation of a secondary material that has sufficient helium capacity or diffusivity at low pressure, and can be synthesized and optimized independently of fuel chemistry. As an additive in fuel pellet fabrication, it would require only minimal elaboration of the normal process. However, the short helium migration distance in uranium oxide requires very small particles of absorbent mixed very uniformly into the fuel. Coating of the fuel particles themselves would solve this uniformity problem, because the uranium oxide itself is prepared in the form of micron-sized particles prior to consolidation. The actual amount of helium to be transported per particle is small, so only minimal intrinsic absorption in the coating would be required.

A process which seems to offer advantages in this application is atomic layer deposition (ALD) on particles [12]. It is based on reaction of two chemical precursors at the surface of a particulate substrate, and differs from more traditional chemical vapor deposition (CVD) in that the surface is exposed to each precursor separately. The deposition is then self-limiting, enabling precise control of film thickness. After exposure to the first reactant, the surface bears a chemisorbed sub-monolayer; the environment is purged of that reactant, and the second reactant is admitted to form a sub-monolayer of film. This reactant is then purged, and the process repeated, building a conformal coating of as many molecular layers as desired on primary particles. Although ALD is typically used on flat surfaces in the electronics industry, for present purposes a fluidized bed reactor is more appropriate; particles are

lifted and agitated by inert carrier gas, so that the bulk properties are those of a fluid. This technique permits excellent control and is scalable to the production rates which would be necessary for nuclear fuel manufacturing.

There are a number of constraints on the chemistry for a coating that facilitates helium transport or capture in nuclear fuel. First, it must be compatible with the nucleonics of the reactor: low neutron absorption and no transmutation into a material which would not sequester helium. Second, the coating must be thermodynamically compatible with the reactor fuel (and to a lesser extent, the cladding alloy) over the expected lifetime of the fuel. Given the high temperature, long time, and small distances involved, even slight chemical reactivity would compromise the function of the coating. The highest temperatures of the nuclear fuel cycle occur during sintering. Sintering temperatures range from 1600 °C to 1800 °C [13–18]. However, a recent study has demonstrated fuel sintering at temperatures as low as 835 °C via spark plasma sintering (SPS) [15]. Lower sintering temperatures open an array of potential materials to be used as fuel additives that could not maintain their favorable properties toward helium sorption upon exposure to temperatures over 1600 °C.

Alumina is an inert metal oxide potentially suitable with CERCER and CERMET nuclear fuels, which are based on ceramic MgO and metal Mo matrices, respectively. The interaction with implanted helium with alumina, MgO, and other inert matrix metal oxides has been examined by van Veen et al. [19] Alumina was chosen for study here because of its compatibility with the promising particle ALD process for distribution of the material around nuclear fuel particles. A comprehensive review of ALD chemistry shows the compatibility of the ALD alumina synthesis process with both uranium oxide and nickel substrates [20]. Alumina has been demonstrated to be thermodynamically compatible with the uranium oxide reactor fuel, i.e., no new phase will form up to 2000 K [21,22]. Also, aluminum's low neutron cross section [23] precludes significant neutron interactions during nuclear fuel operation and storage. In fact, fuels directly incorporating aluminum for, among other advantages, improved thermal conductivity have been previously investigated [24,25]. Helium transport properties in alumina can be understood with complementary data such has been previously obtained by van Veen [19] and Hurst [26]. Finally, there are indications that alumina surrounding nuclear fuel particles can improve mechanical stability of the fuel composites [15]. In the future, ALD processes may be developed for inert metal oxides with greater thermal stability, such as yttria-stabilized zirconia, or metal silicates. This study, however, focuses exclusively on nickel particles as surrogates for uranium oxide nuclear fuel and alumina as a first material for examination to facilitate helium transport and retention.

## 2. Experimental and simulation methods

### 2.1. Materials

Nickel particles (diameter ~3  $\mu\text{m}$ , 99.7%, Aldrich Chemical Company) were used as surrogate substrates for uranium, since helium is expected to behave comparably in alumina on both nickel and uranium oxide particles. ALD alumina also shows comparable

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