A Thin-Alumina Film as a Tritium Adsorption Inhibitor for Stainless-Steel 316

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Thin coatings of Al_2O_3 on stainless steel have been reported to suppress tritium permeation compared to uncoated steel.[1–3] However, these films are not dense; they contain microcracks, and have the potential for embedded water molecules in the film. Reducing the cracks in the alumina film may prove to further reduce permeation, and for surfaces with highly dense and uniform coatings, the permeation reduction may be improved substantially. Atomic layer deposition (ALD) is a vehicle to produce conformal, high-integrity films on hydroxylated surfaces with complex topographical features. Depositing alumina using trimethylaluminum and water is one of the most widely studied ALD reactions because of its viability as a high-κ dielectric thin-film coating. ALD of Al_2O_3 has been shown to produce conformal films with little to no surface defects as a result of the self-limiting reaction and monolayer growth mode. Atomic-layer–deposited alumina was used in this work to understand its effect on tritium absorption and to measure the tritium distribution in stainless-steel 316 (SS316) under the coating.

Samples of unmodified SS316 stock had approximately 0.86 mm of the surface machined away to remove any surface imperfections that can arise during manufacturing. These samples had an average surface roughness of 300±50 nm and are referred to from this point as 300-nm SS316. A subset of the 300-nm SS316 samples was mechanically polished to a high-mirror finish, where the average surface roughness was 5±1 nm, and is referred to as 5-nm SS316. Several polished samples were further treated by depositing 38.5±1 nm of Al_2O_3 using the ALD process and an ozone pretreatment to enhance the reactivity of the native surface oxide to the ALD reactants. These samples are referred to as ALD and have the same surface roughness as the underlying polished samples (5±1 nm). All samples were exposed to 0.5 atm of tritium gas for 24 h at room temperature. Subsequently, the samples were removed and stored in an airtight storage pod under dry helium until retrieved for the experiment.

Temperature-programmed desorption was used to determine the total quantity of tritium retained by the stainless-steel samples. The tritiated sample is placed in an oven where dry argon is purged over the sample into one of two bubblers containing water. The sample is heated to 900±1° for several hours during which the desorbed tritium is transported by the dry argon into the bubblers. The primary tritium species (HTO) is captured in the first bubbler (capture efficiency >99%), and any carryover resulting from evaporation is captured in the second bubbler. After 3 h at room temperature, the sample is allowed to cool, and the quantity of desorbed tritium is determined using liquid scintillation counting (LSC) techniques. Tritium-concentration profiles in the deposited film and metal substrate were also measured using a combination of surface washes and acid etching of stainless steel. The surface wash and acid etching procedure are reported elsewhere.[4,5] The etching procedure for the samples coated with Al_2O_3 was modified by using a selective NaOH etch that does not etch the steel substrate. The resulting solutions were neutralized to a pH = 0, mixed with an Ultima Gold^{TM} liquid scintillation cocktail, and counted by LSC techniques using a low pH calibration curve.

The total quantity of adsorbed tritium indicates that the surface modification had influenced the total tritium adsorbed by the sample. The results of the TPD experiments are shown in Fig. 1. The data indicate that reducing the surface roughness by a factor of ~150 leads to a reduction in the total quantity of absorbed tritium, relative to the 300-nm SS316 samples. Similarly, the ALD-coated steel samples also see a decrease of ~27%. These data indicate that the ALD coating on the polished SS316 does not inhibit the absorption of tritium any further than the underlying polishing. This is likely caused by the large fraction

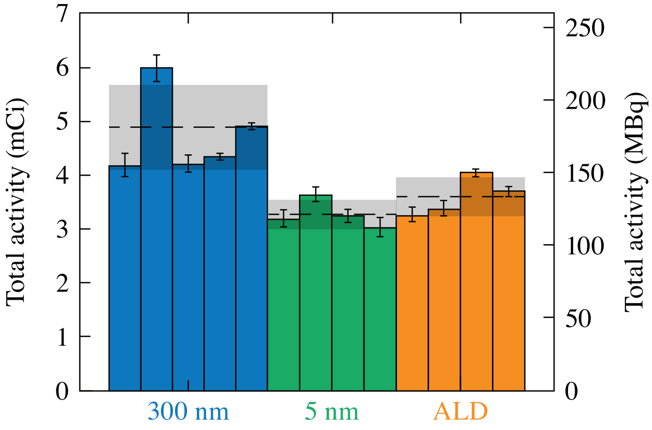

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Figure 1
TPD results for the unmodified (blue bars) and modified surfaces, 5-nm SS316 (green bars) and ALD (orange bars). Each bar represents an individual sample, with the mean as dashed lines and ±1σ indicated by the shaded region for each sample finish.

of $Al(OH)_2$ species present in the deposited film, which increases the total number of hydrogen binding sites relative to a pure Al_2O_3 surface film. The increase in the hydroxyl density in the deposited film increases the apparent solubility of hydrogen in the film as a result of isotope exchange with hydrogen in the hydroxides. The TPD data give an insight into the total quantity of tritium in the samples; however, the data do not speak to the distribution of tritium in the metal.

The results of the selective etching for the ALD-coated steel are shown in Fig. 2. The data suggest that high concentrations of tritium exist in the Al_2O_3 layers and that the concentration drops significantly at the steel interface. In the near-surface region ($x <$ 1 μm), the SS316 concentration is constant until a sharp drop is observed around 600 nm. To compare the concentration profiles of the ALD samples to the uncoated SS316 samples, the profiles for the uncoated steel (5 nm and 300 nm) are shifted by the alumina layer thickness (38 nm) in the concentration profile. The results show two large differences between the ALD and SS316 results. First, the ALD film contains less surface tritium compared to the uncoated samples. The second difference occurs in the near surface of the steel (~700 nm). Here, the tritium concentration is 200× less in the ALD-coated sample relative to the uncoated SS316 sample. This suggests that tritium diffusion into the metal bulk is lowered by coating steel with alumina. Even though the 5 nm and ALD samples retained the same total quantity of tritium, the distribution of the tritium in the samples is quite different. Future work will focus on making the alumina layers more ideal to determine if these films can be used as a tritium diffusion barrier on SS316.

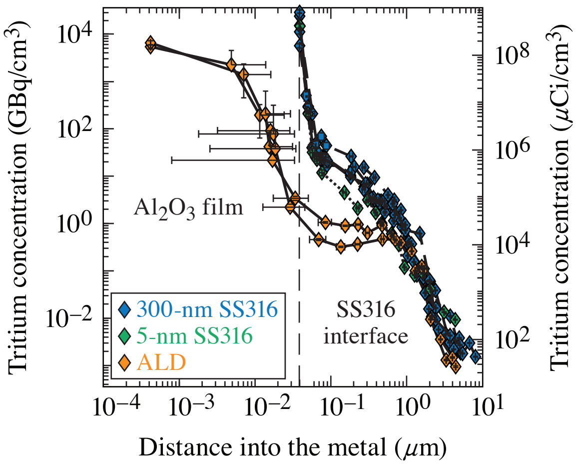

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Figure 2
Tritium concentration profiles for 300-nm SS316 (blue), 5-nm SS316 (green), and ALD Al_2O_3 (orange) (Ref. 4). The uncoated samples are shifted to account for the deposited film on the ALD samples. The SS316 interface begins at the 38 nm and is indicated by the vertical dashed line.

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