Investigation of Inorganic Hydrophobic Filter Material for Nuclear Material Transportation and Storage Containers– 16640

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ABSTRACT

Los Alamos National Laboratory has begun development of hydrophobic or super-hydrophobic inorganic filter materials that resist water ingress after exposure to radiation and/or elevated temperature. Filters that are currently available depend on carbon composites and/or organic polymers for their water resistant/hydrophobic properties to minimize water ingress. However, facility and transportation accident scenarios often include fire, impact and subsequent water spray or flooding conditions. A purely inorganic hydrophobic filter material could have enhanced resistance to fire and radiation damage, and continue to minimize water ingress after such an accident. Such filters could broaden the use of filtered containers in the transportation and storage of nuclear materials, and could have broader implications in other industrial applications. The goal is to create a porous inorganic material with hydrophobic properties that maintains or exceeds the current performance criteria for particulate filtration efficiency, pressure differential, air flow and hydrogen diffusion. The materials developed in this project will be evaluated for use as potential enhancements to the SAVY 4000 nuclear storage container that is becoming widely used around the DOE complex. This paper will describe the methods and results of this investigation.

INTRODUCTION

A recent paper in the Journal Nature Materials[1] reports that rare earth oxide ceramics when pressed into pellets show a high degree of hydrophobicity, and it is proposed that coating the aluminosilicate filters with a hydrophobic rare earth oxide may be a viable path towards replacing the low melting point PTFE membrane. It is proposed to develop a purely inorganic membrane or filter material would have enhanced radiation and high temperature stability. Such a material would have important implications for criticality safety because the materials that are currently used (PTFE and carbon) would be destroyed after a fire insult and could be susceptible to radiation damage when used inside a glovebox. These filters are currently being credited in the TA-55 plutonium facility to prevent water ingress into nuclear material storage containers (both inside and outside of gloveboxes) and thus mitigate the risk of a criticality accident in the event of the activation of the fire sprinkler system.

METHODS AND RESULTS

We have synthesized the CeO_2 thin films listed in Table 1 using the polymer assisted deposition (PAD) technique described in the scope-of-work. In addition, we have measured XRD to confirm the presence of CeO_2, SEM to determine surface structure, and contact angles to measure hydrophobicity. The original work scope requested one CeO_2 film to be synthesized on yttrium stabilized zirconia (YSZ) substrate, with subsequent XRD, SEM and contact angle measurements (CeO_2 on YSZ, 1 coat). These results showed the presence of CeO_2 *via* XRD and a contact angle of 60°, which is at the lower end of what is considered hydrophobic. The SEM on this initial film showed holes in the film (Figure 1), and it was decided to grow a second layer to fill gaps in the film (CeO2 on YSZ, 2 coat). The second coat resulted in a lower contact angle, 40°, possibly due to reducing surface structure responsible for hydrophobic behavior.

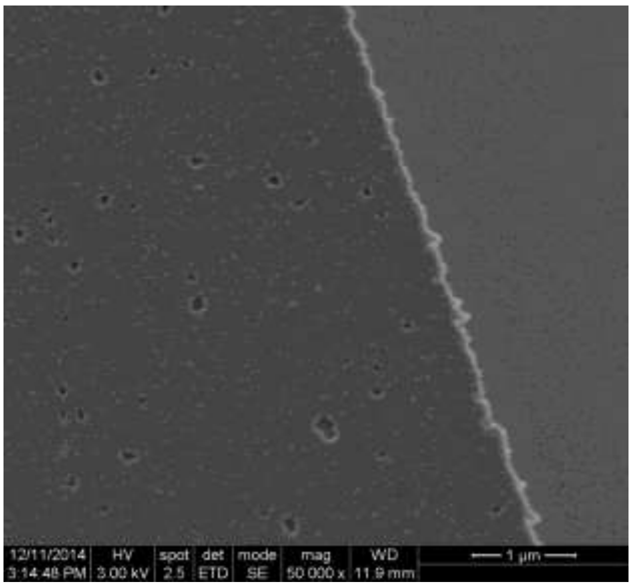

Figure 1. SEM image of 1 coat CeO_2 on YSZ showing holes in film. The uneven edge on the right side of the image is the boundary between the CeO_2 film (left) and the YSZ substrate (right).

At this point it was decided to look at archival CeO_2 films that we had from a previous project. These films were UV cleaned and contact angles were measured. It was found that CeO_2 grown on lanthanum aluminum oxide (LAO) gave high contact angles, > 90°, indicative of strong hydrophobic character (Table 1). In a third case the contact angle only measured 76°, presumably due to the alternate substrate preparation technique of sonication *versus* UV cleaning. Also, a CeO_2 film on c-cut sapphire gave a contact angle of 60°. Based on these results, we believe the underlying structure of the substrate is not only templating the growth of the ceria lattice, but also determining the mesoscopic structure of the film. It is known that pillared and grooved surfaces enhance hydrophobicity through reduction of surface-water contact area and geometry effects[1]. An AFM of one of our ceria films on LAO show surface structure consistent with pillars and/or grooves (Figure 2). This surface structure may be the cause of the enhanced hydrophobicity observed in ceria films grown on LAO.

Table 1. Summary of experimental data from CeO_2 thin films grown on various substrates.

Sample	Substrate prep	Contact angle (°)
CeO_2 on LAO, #1	UV clean	97
CeO_2 on LAO, #2	UV clean	94
CeO_2 on LAO, #3	Sonicate in ethanol	76
Bare LAO	UV clean	< 20
CeO_2 on c-cut sapphire	UV clean	60
CeO_2 on YSZ, 1 coat	UV clean	60
CeO_2 on YSZ, 2 coat	UV clean	40
Bare YSZ	UV clean	< 20

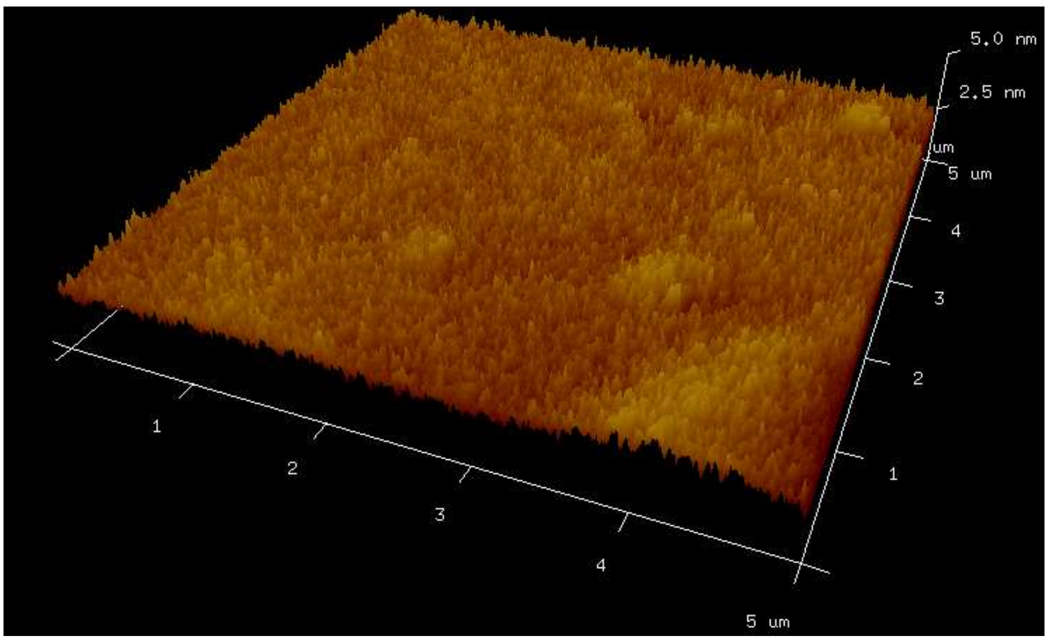

Figure 2. Atomic force microscopy (AFM) image of CeO_2 film on LAO substrate showing pillars and groove-like structures.

Additional work has been done in the design of a fixture, Figure 3 & Figure 4, that will test the Fiberfrax® filter material samples in the working configuration for its ability to resist water penetration. This fixture will allow us to determine the functionality of the CeO_2 coatings and help make a determination of feasibility. This fixture has been manufactured out of hard plastic using a 3D printer, and though the plastic fixture was intended to be a prototype, it has been tested and determined to be fully functional. A fixture developed under a separate study (funded by the Nuclear Safety R&D program) was used (Figure 5) along with the plastic prototype developed on this project. The capability to test water ingress is illustrated by the preliminary water ingress test results listed in Table 2 using both

Hagan (carbon filter) and SAVY (Fiberfrax filter with PTFE membrane) containers for a period of 2 hours with water pressures ranging from 1 ft to 5 ft. This capability development (leveraged with RTBF Storage funds) will be used to test the materials as they are developed.

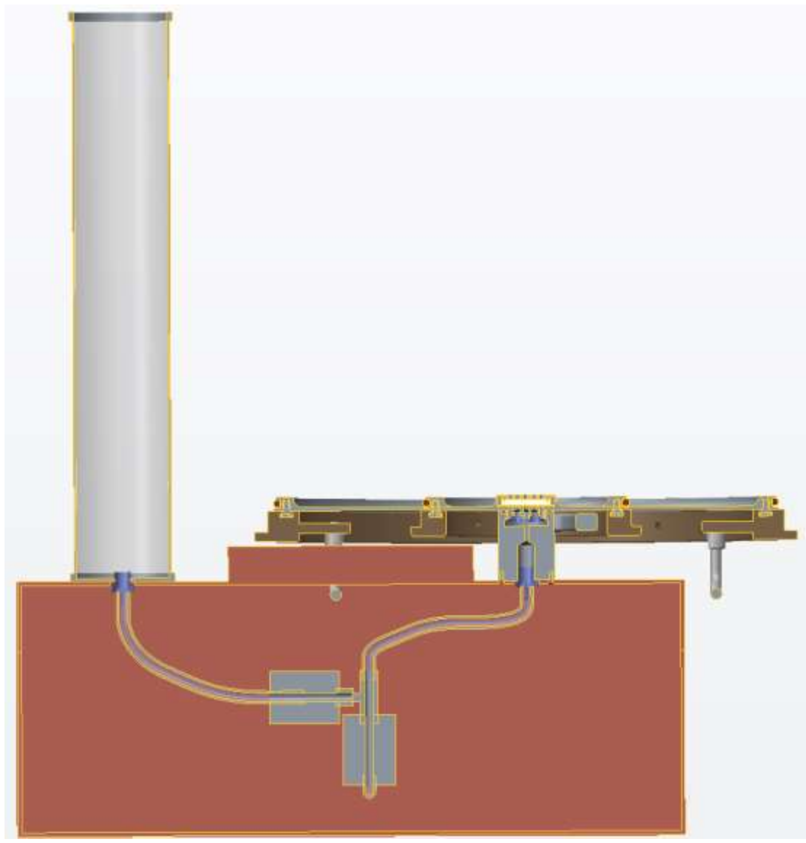

Figure 3: Cross section view of water penetration apparatus.

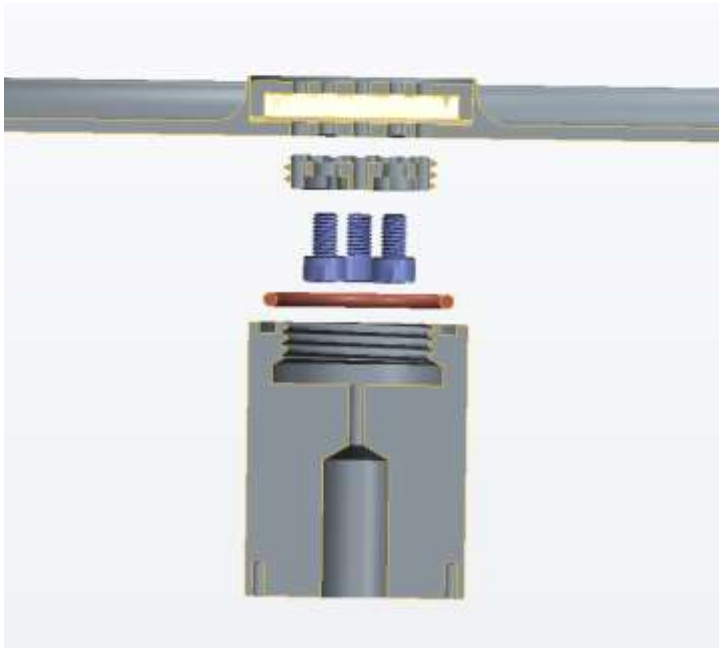

Figure 4: Exploded view of water penetration fixture

The aluminosilicate fibers present in Fiberfrax present a new substrate structure for the growth of ceria films. However, due to the latex binder used in the Fiberfrax filter material it is necessary to eliminate it by heating it before spin-coating or rotary evaporation of the aluminosilicate. Neither technique produced a hydrophobic coating, although XRD did show that a CeO_2 film was present. When a drop of water was placed on the treated materials it was immediately drawn into the filter material. Given this observation it was determined that testing these membranes using the test fixture was not necessary.

An important conclusion from these studies is that the determining factor in creating a hydrophobic coating or material is to focus on the micro structure. Small pillars on the surface of a material have been shown to increase the contact angle of materials.[3] Thus, it is insufficient to create a CeO2 film by itself, but it must be a film that has the particular microstructure that leads to hydrophobicity.

Table 2: Preliminary Water Ingress Test results for Hagan and SAVY Containers

Serial#	Container Size	Container Type	Height (in.)	Increase in Wt. (g)	Pre-Test Pressure Drop (in H_2O)	Post-Test Pressure Drop (in H_2O)	Start Time	End Time
08/07-967-019	5Qt.	Hagan	12.5	0.5	0.765	Maxed	10:01:00 AM	12:01:00 PM
09/06-634-013	5Qt.	Hagan	12	1.1	0.563945	4.396	9:32:00 AM	11:32:00 AM
08/02-719-013	5Qt.	Hagan	24	213.5	0.8709	26.762	12:46:00 PM	2:48:00PM
08/02-839-013	5Qt.	Hagan	18	14.8	0.704	18.73	7:18:00 AM	9:20:00 AM
09/06-520-013	5Qt.	Hagan	28	11.8	0.796	14.99	9:45:00 AM	11:47:00 AM
091205141L	5Qt.	SAVY	13	21	0.653927	Maxed	10:01:00 AM	12:01:00 PM
071203144L	3Qt.	SAVY	6.125	2.3	0.7136	Maxed	1:30:00 PM	3:30:00 PM
071203144L	3Qt.	SAVY	60	3.5	0.7136	42.819	4:25:00 PM	12:25:00PM
071203160L	3Qt.	SAVY	60	0.7	0.6762	8.029	1:01:00 PM	3:02:00 PM
091205141L	5Qt.	SAVY	60	188.9	0.683	42.819	7:32:00 AM	9:32:00 AM
011305006L	5Qt.	SAVY	60	0.8	0.655709	4.4434	10:00:00 AM	12:05:00 PM
121103038L	3Qt.	SAVY	60	1.9	0.7092	8.029	12:25:00 PM	2:29:00 PM
081305135L	5Qt.	SAVY	60	1.7	0.585	26.76	7:08:00 AM	9:10:00 AM
111103029L	3Qt.	SAVY	60	3.7		37.47	10:48:00 AM	12:50:00 PM

CONCLUSIONS

The initial stage of this work demonstrated that CeO_2 (ceria) films grown using the polymer assisted deposition (PAD) technique can produce highly hydrophobic surfaces given the proper substrate. The PAD technique has also been used to produce ceria coatings on Fiberfrax ceramic filters (the material currently used in the SAVY 4000 filter), which have been characterized to determine hydrophobicity. The ceria coated Fiberfrax materials, made in two different ways, were determined to have very low hydrophobicity. An important conclusion from these studies is that the determining factor in creating a hydrophobic coating or material is to focus on the micro structure, not the coating itself. With this new understanding, the focus will shift to the development of copper oxide hierarchical structures.

FUTURE WORK

The focus will be shifted to developing functionalizing copper metal with hierarchical oxide surface structures based on a literature report of superhydrophobicity.[3] The high melting point of copper (~1000°C) and the inorganic nature of the oxides could lead to a temperature and radiation resistant material that is capable of repelling water and allowing the passage of gases. The following specific tasks are proposed and will be prioritized according to available funding:

1) Repeat literature synthesis of copper oxide hierarchical structures on copper plate. Image structures using SEM, XRD, and measure contact angles.

2) Transfer copper oxide hierarchical structure chemistry to commercial sintered copper filters. There are many options made from both sintered powders and wires down to tenths of a micron pore size. Image structures using SEM, XRD, and measure contact angles. Test filters for water and vapor transport.

3) Transfer copper oxide hierarchical structures to copper sputtered (or vapor deposited) fiberfrax filters. Image structures using SEM, XRD, and measure contact angles. Test filters for water and vapor transport.

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