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Characterization of Environmental Stability of Pulsed Laser Deposited Oxide Ceramic Coatings

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Abstract

A systematic investigation of candidate hydrogen permeation materials applied to a substrate using Pulsed Laser Deposition (PLD) has been performed. The investigation focused on application of leading permeation-resistant materials types (oxide, carbides, and metals) on a stainless steel substrate. and evaluation of the stability of the applied coatings. Type 304L stainless steel substrates were coated with aluminum oxide, chromium oxide, and aluminum. Characterization of the coating-substrate system adhesion was performed using scratch adhesion testing and microindentation. Coating stability and environmental susceptibility were evaluated for two conditions—air at 350°C and Ar-H_2 at 350°C for up to 100 hours. Results from this study have shown the pulsed laser deposition process to be an extremely versatile technology that is capable of producing a sound coating/substrate system for a wide variety of coating materials.

Introduction

The Savannah River Site uses components for heated tritium handling and storage service that have been treated with a proprietary diffusion aluminizing coating process to apply permeation barrier coatings to heated tritium handling equipment. The reproducibility of the coating quality and microstructure using the “Alonizing” process has been inconsistent. In recent years, the complexity of the components has increased and the Alonizing process was not suitable to coat items like the tube in tube (TnT) thermal cycling absorption process (TCAP) unit. Alonizing would result in too variable a coating thickness and may have consumed to great a proportion of the thin walled tubing. Alonizing was also not suitable for coating the helical heat exchanger coil for the tritium consolidation project. The size, complexity, and desire to not heat this component to the required coating temperature resulted in the use of a new coating without much documentation of its permeation resistance.

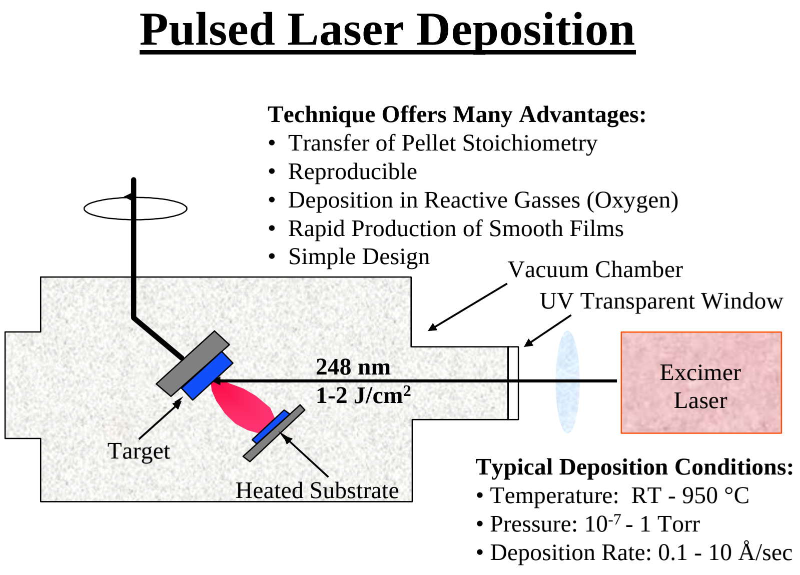
The pulsed laser deposition technology has been the focal point of a Plant Directed Research and Development program that was initiated during the 2nd quarter of FY02. The focus of this program was to demonstrate the versatility of the PLD technology with respect to the ability to apply a wide range of coating materials—metals, oxide, carbides, nitrides, glasses, etc, and to evaluate the stability of the applied PLD coatings. The PLD technology has been previously demonstrated to be capable of processing various multi-component complex electronic, optoelectronic, and superconducting thin film materials. The PLD process provides for controlled microstructures, controlled thickness, and uniform application over complex substrates that could achieve desired permeation resistance performance in hydrogen/hydrogen isotope handling and storage components. Additionally, this technology offers the possibility to both modify the surface of the materials to be coated to enhance adhesion, wear, and corrosion in order to tailor the response of the materials system—substrate and coating—to achieve the desired response under the environmental conditions expected. Pulsed laser processing is a versatile technology that has great potential for a variety of applications

A systematic investigation has been performed to use PLD to create coating/substrate systems and to evaluate their feasibility including mechanical stability and efficacy for use on hydrogen /hydrogen isotope system components.

Background on Pulsed Laser Deposition

The pulsed laser deposition process is both conceptually and experimentally relatively simple. Pulsed laser deposition is largely an inorganic thin film deposition technique which was heavily practiced from the mid 80's into the early 90's for the deposition of complex, multi-component materials in thin film form (ceramics, superconductors, metals, etc.) [1-5]. Figure 1 shows a schematic of the fundamental process. PLD typically utilizes the output of a pulsed UV laser (193 and 248 nm) focused onto a solid target which rapidly heats, vaporizes and creates nearly atomic (partially ionized) vapor that is deposited upon a heated substrate, typically another ceramic, metal or glass, with retained stoichiometry. Typical deposition pressures range from 50-400mTorr in the presence of a backfill gas, although depositions have been performed from 10^{-9} Torr (vacuum) to 1Torr routinely. In general, the backfill gas plays an active role in the deposition process in several ways. First, the backfill gas confines the expanding plasma, which leads to a higher growth rate at the substrate. Second, the gas may be used to reactively grow several classes of materials such as nitrides, oxides, and sulphides. Finally, the backfill gas can be used to thermalize the plasma and assist in nanoparticles formation based on overall pressure and backfill gas molecular weight.

PLD offers an excellent experimental technique for investigating the fundamentals of film deposition and the properties of new materials. Table 1 provides a brief listing of materials that have successfully been deposited via PLD. The listing in Table 1 comprises superconducting materials (YBCO), wide band gap semiconductors (ZnO, TiO, Nitrides, Diamond), cold cathode field emitters (Diamond Like Carbon (DLC), Diamond, carbon nanotubes), tribological materials (DLC, TiC) and metals. Given the simplicity of the process there are almost no restrictions on the target material to be used--PLD with liquid target materials has been demonstrated [6-8] and even PLD of solid nitrogen and methane has been probed experimentally [9]. Another advantage of PLD is that it allows for the possibility of introducing reasonably high pressures of background gas into the vacuum chamber. This is often necessary when depositing multicomponent films with specific stoichiometry. It also enables creation of new materials during deposition, e.g. growth of nitrides or oxides from PLD of the respective single elemental materials in a background pressure of either oxygen or nitrogen. PLD is a rapidly developing field and the number of materials deposited by the technique is quickly expanding.



Pulsed Laser Deposition

Technique Offers Many Advantages:
- Transfer of Pellet Stoichiometry
- Reproducible
- Deposition in Reactive Gasses (Oxygen)
- Rapid Production of Smooth Films
- Simple Design

Typical Deposition Conditions:
- Temperature: RT - 950 °C
- Pressure: 10^{-7} - 1 Torr
- Deposition Rate: 0.1 - 10 Å/sec

Figure 1. Schematic of a basic PLD system.

Table 1 Variety of materials deposited with PLD

Materials Class	Compounds
High-temperature Superconductors	YBa2Cu3O7 BiSrCaCuO TlBaCaCuO MgB2
Oxides	SiO2
Carbides	SiC
Nitrides	TiN
Ferroelectric materials	Pb(Zr,Ti)O3
Diamond-like carbon	C
Buckminster fullerene	C60 C
Polymers	Polyethylene, PMMA
Metallic systems	30 alloys/multilayers FeNdB

Experimental Approach

PLD Coatings

Candidate coating materials were chosen based on previous research focused on hydrogen permeation barrier materials. The following coating materials were selected for demonstration—Al_2O_3, Al, and Cr2O3. These materials were chosen based on the following reasons: 1) Al—the current family of Alonized™ coatings used for Tritium service applications are based on a packed bed Aluminide coating process that reacts aluminum with the surface of the stainless steel to form a multilayered coating of varying aluminum content, 2) Al_2O_3—it has been speculated that in the case of aluminized coating the increased permeation resistence displayed by these coatings has been attributed to the outer surface layer (1-5μ) of aluminum oxide that is inherent on packed bed aluminized coatings, 3) Cr_2O_3—chromium oxide was selected based on two driving factors—chromia has previously been shown to be a moderately effective hydrogen isotope permeation barrier; depending on oxidation conditions chromia makes up the major component of the oxide scale formed on stainless steel alloys and this chromia scale is typically a non-spalling scale that maintains structural adherence.,

A contract was established with Professor James Fitz-Gerald from the Materials Science and Engineering Department at the University of Virginia for PLD coating services. These coating materials were applied to 1.25" diameter 304L stainless steel substrates 0.030-0.036" thick that had been polished to a 1μ finish. The PLD coatings were applied using a Lambda-Physik 248nm excimer laser focused onto a rotating target of the desired coating materials. The background environmental pressure ranged from 50-200mTorr with the background gas being either Ar or O_2 depending on the desired coating material.

PLD Coatings Microstructural and Surface Characterization

Characterization of the coating-substrate samples was performed using SEM and AFM. A JEOL 6700F field emission SEM was employed to document the baseline microstructure and condition—cracking, spallation, ablation masses and pits- operating at an acceleration voltage between X and Y at magnification up to 100,000X. Atomic force microscopy of the coating flaws and roughness for both the baseline and exposed condition was performed using a Digital Instruments Mulitmode Nanoscope with a SiN probe in tapping and contact mode.

Environmental Exposure

Environmental exposure testing was conducted in order to evaluate the stability of the PLD coatings. Testing was performed using flowing air and mixed Ar-H_2 at flow rates from 1-5scfh. These samples were heated at 350°C and evaluations of the microstructural evolution for hold time up to 30 hours in Ar-H_2 and 100 hours in air were performed using AFM, Surface Topography Analysis (STA)—roughness and power spectral density--, and composite microhardness.

Adhesion Testing

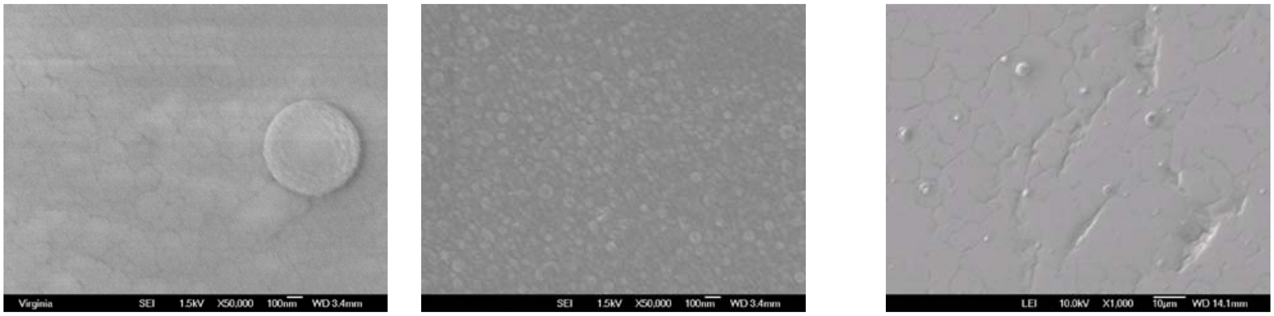
Adhesion testing was performed using two techniques—microindentation and scratch testing. The microindentation testing was conducted using a standard Buehler microhardness tester with a Vickers indenter. Scratch testing was completed using a Nanoindenter® XP with a Berkovitch indenter. Five-minute epoxy is used to adhere the test sample to a microscope slide. The microscope slide is glued onto an aluminum mount, making sure that the test surface is rigidly mounted. The scratch is generated by the motion of the table that is carrying the sample while the indentation head controls the load applied on the sample via the indenter. Five scratches were run on each sample and the data averaged.

Results and Discussion

A Characterization of As-Deposited PLD Coatings

One of the major focal points for this development program was to evaluate the ability of the PLD technology to apply a range of coatings materials maintaining stoichiometric compositions for multi-component system and to do so with minimal coating defects. To this end, as-deposited coatings have been characterized using scanning electron microscopy (SEM) optical microscopy, and atomic force microscopy (AFM).

Scanning electron microscopy of the as-deposited coatings were performed using field emission JEOL 6700F with energy dispersive spectroscopy (EDS). Figure 2 displays the SEM photomicrographs for Al, Cr2O3, and Al2O3. From these photomicrographs an estimate of the coating thickness was also determined using the SEM by imaging the coating –substrate edge—Figure 3. The coating thickness for all the samples evaluated was estimated to be 1-2µ..



(a) (b) (c)

Figure 2. Field Emission Scanning Electron Micrographs of as-deposited PLD coatings: a)Al_2O_3, b)Cr_2O_3, and c)Al

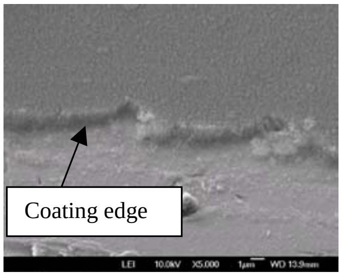
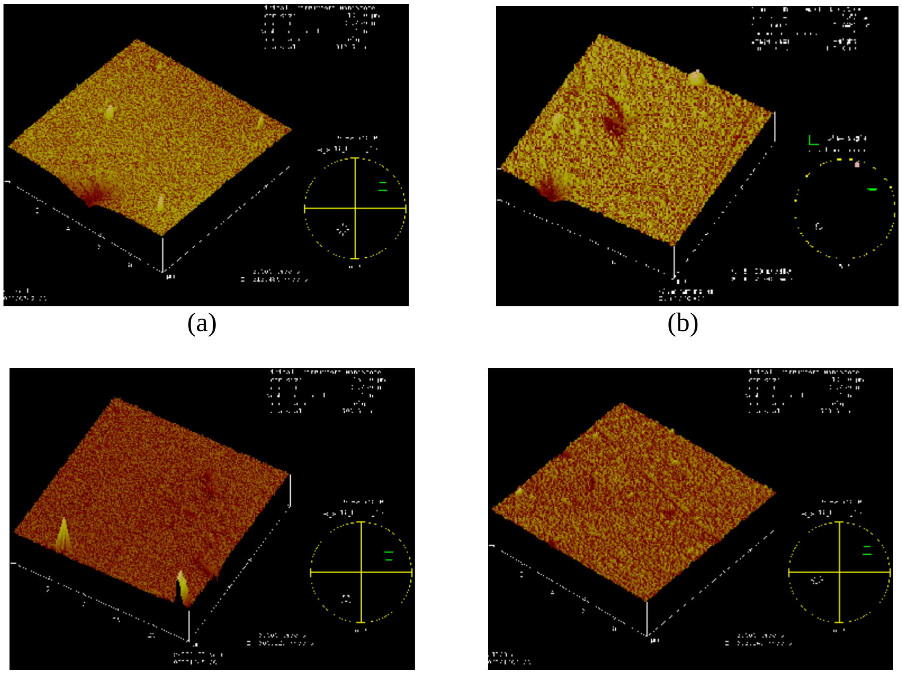


Figure 3 Representative edge on FSEM at 50,000X for Estimating Coating Thickness

Atomic Force Microscopy (AFM) of the coatings surfaces provides a more direct measure of the surface topography/morphology for the as-deposited films. Figure 4 shows representative AFM images from the as-deposited coatings. The as-deposited coatings appear to be uniform in deposit without large disparity in thickness. Additionally, little evidence of coating damage or holidays is discernible. Lastly, the AFM images show no cracking that can occur due to shrinkage and thermal stresses caused as a result of the coating deposition process.



(a) (b)

(c) (d)

Figure 4 Atomic Force Microscopy of Stainless Steel Substrate and As-deposited Coatings: a)304L, b)Al on 304L, c)Cr_2O_3 on 304L. d)Al_2O_3 on 304L—20µ X 20µ scan area.

Coating Adhesion and Stability

One of the critical phenomena associated with the success of coatings and coated materials is the adhesion of the coating under the condition of operation. An evaluation of adhesion in a coating-substrate system provides a measure of the interfacial bonding and is related to the interfacial area and intrinsic coating stress. An initial attempt to assess coating adhesion was made using standard microhardness testing equipment since that equipment is readily available in most metallurgical testing facilities. However, as shown in Figure 5 with coatings of only 1-2µ in thickness the loads available on the microhardness tester were too large and any information to be gained concerning the coating or the coating-substrate interface were obscured by the response from the much thicker 304L substrate. Thus, another more specialized test method was needed to provide more sensitivity for these thin coating samples. The scratch adhesion test method provides a quick and convenient test that can be used to measure a variety of coating-substrate systems with varying thickness and hardness. In a scratch test a diamond stylus is drawn across the surface of the coating-substrate sample under a continuously increasing load until the coating detaches from the substrate. The load at which the coating is separated from the substrate is defined as the critical load L_c and provides a qualitative measure of adhesion strength.

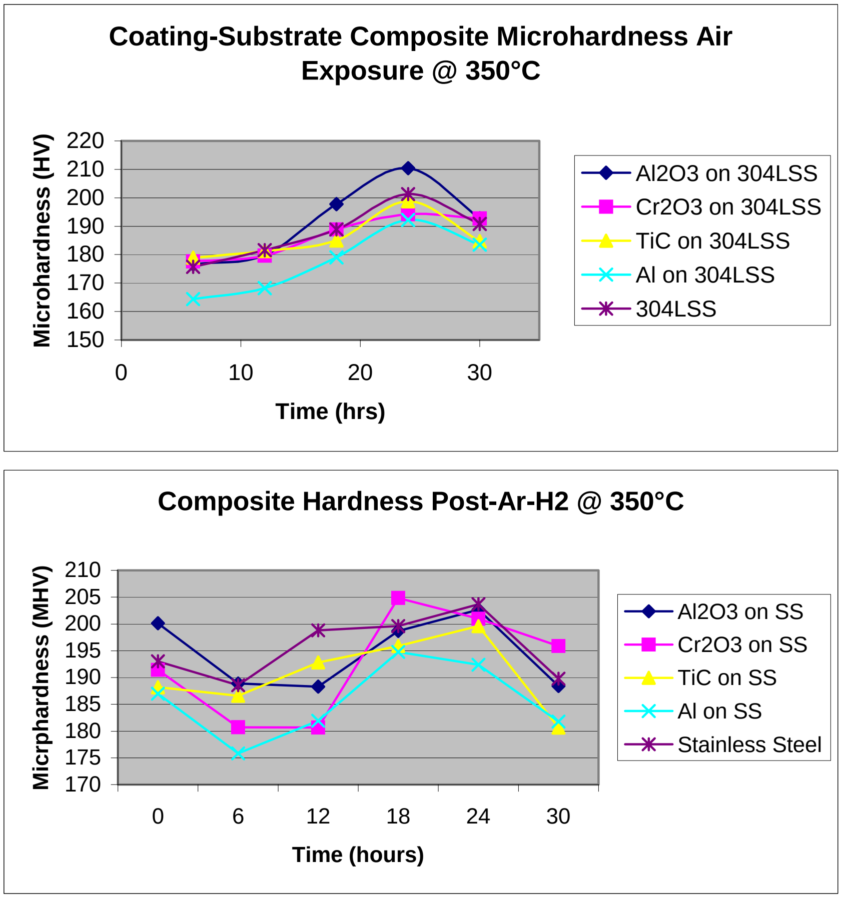


Figure 5 Microhardness Measurements at 50gm load and 5s Residence Time for Coating-Substrate Samples.

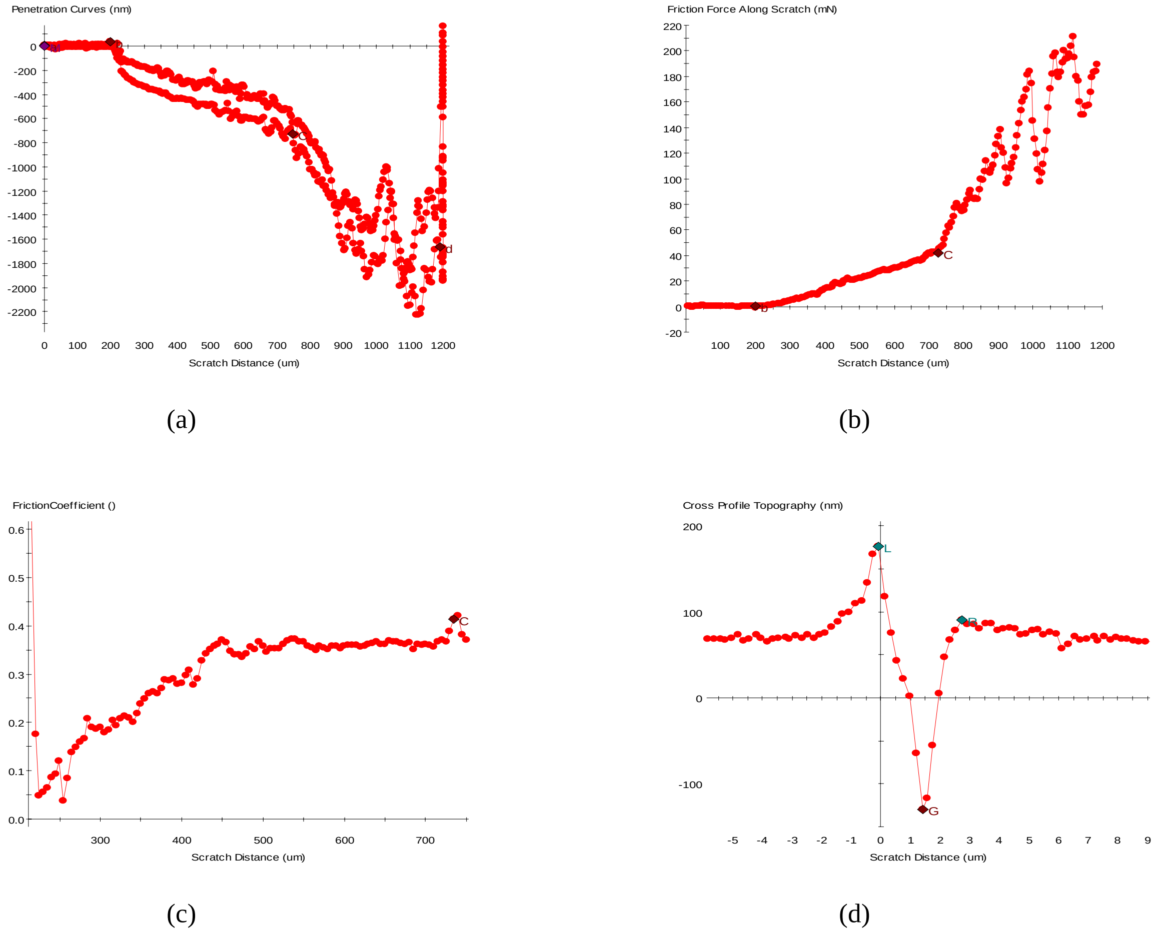
Scratch adhesion testing was conducted for representative coating samples applied using the PLD technique. These samples were evaluated under the following conditions:

Scratch speed: 0.1µm/s to 2.5mm/s
Scratch length: 1mm
Maximum lateral force: 250mN (All orientation)
Maximum force resolution: 2µN
Noise level: 300 µN (without contact) lateral force
Scratch orientation: 0º to 360º
These tests were done with a Berkovich indenter and five scratches were performed on each sample.

There are four steps involved in conducting the scratch test:

1. An initial profile of the surface is realized under a very small load (100 µN), in order to have the original morphology of the surface before the scratch.
2. Then, along the same path, the normal load is increased from 0mN to 200mN (30mg).
3. A final profile is realized under a very small load (100 µN), to measure the residual deformation in the groove.
4. A cross profile gives the shape of the section of the groove and helps evaluating the plastic deformation. The cross profile was done along the scratch at the point that had a load of 5mN during the scratch.

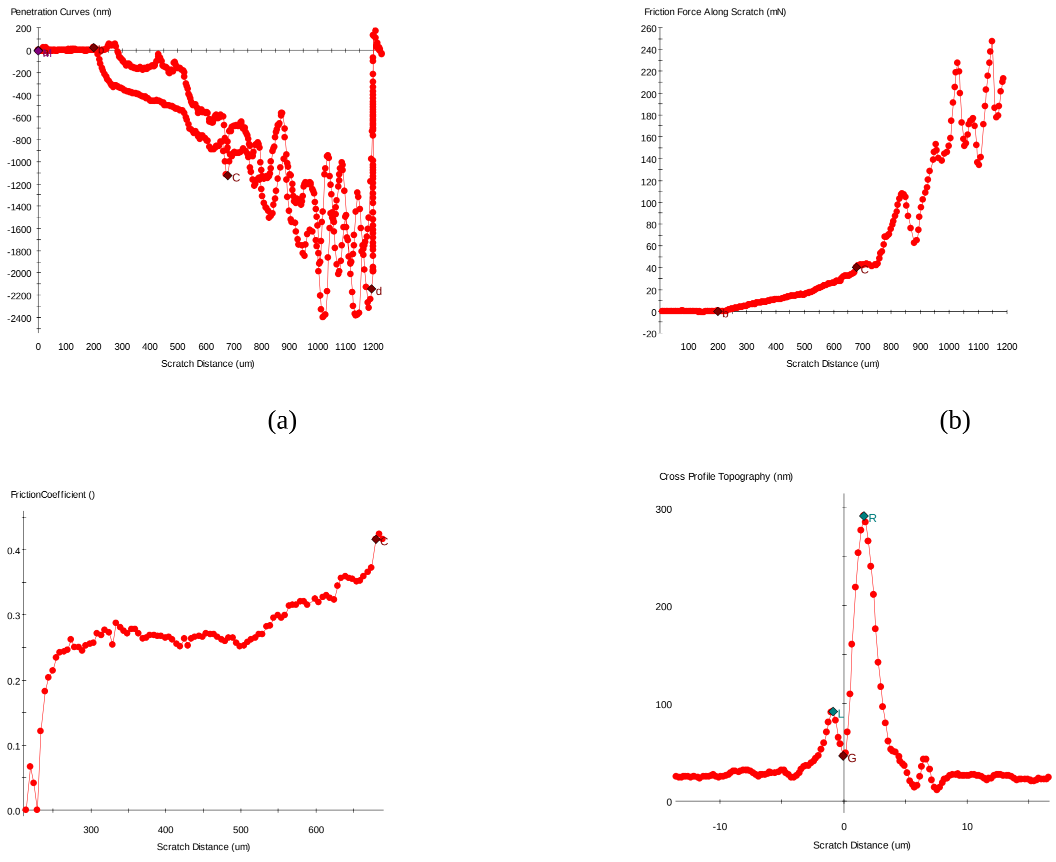
The scratch adhesion data for Al_2O_3 and Cr_2O_3 on 304L substrates are presented herein. Results of the tip penetration, tangential force, friction coefficient, and cross-profile @5mN for the Al_2O_3 and Cr_2O_3, on 304L are shown in Figure 6 and Figure 7.



(a) (b)

(c) (d)

Figure 6 Scratch adhesion data (a) tip penetration, (b)tangential force, (c) friction coefficient, and (d) cross-profile @5mN for Al_2O_3 on 304L.



(a) (b)

(c) (d)

Figure 7 Scratch adhesion data (a) tip penetration, (b)tangential force, (c) friction coefficient, and (d) cross-profile @5mN for Cr_2O_3 on 304L.

Alumina and chromia were both selected for evaluation using the scratch adhesion test because of both of their unique properties in the potential application of hydrogen and hydrogen isotope permeation barriers. Alumina has been previously shown to have a high permeation resistance to hydrogen and has also been considered major factor in the excellent performance of intermetallic aluminide permeation barrier coatings. Chromia in a similar nature was evaluated due its possible use as a self-repairing coating on stainless steel substrate. However, due to the brittle nature of oxide ceramics and also due to the marked difference in Coefficient of Thermal Expansion (CTE) between these coating and the 304L substrate adherence or structural stability of the coating was of great concern. A more ductile aluminum alloy was also evaluated in order to serve as a comparison. From the scratch data presented in Figures 5 6-7, a summary of the adhesion properties for these coatings has been determined and is presented in Table 2.

Table 2. Summary Adhesion Data for Alumina, Chromia, and an Aluminum Alloy on 304L

Material	Critical Load mN	Penetration Depth At Critical Load nm	Scratch Width um	Total Height Of the Groove nm	Residual Scratch Depth nm
Alumina	106.842 ± 3.644	673.661 ± 38.187	3.027± 0.202	258.69 ± 16.604	169.416 ± 86.806
Chromia	103.112 ± 3.577	1011.384 ± 98.261	3.008 ± 0.914	223.603 ± 78.756	87.732 ± 120.371
Al-Alloy	75.275 ± 3.198	1178.104 ± 707.53	2.415 ± 0.128	273.284 ± 30.052	142.542± 38.441

In scratch testing the onset of interfacial delamination is displayed by a sharp increase in the friction coefficient. The normal load at which this sudden increase occurs is called the Critical Load, L_c, and provides an invaluable measure of coating adhesion when comparing different coating materials applied using the same process on identical substrates. For the case of the candidate alumina and chromia coating materials, comparison of these two materials with each other and also with PLD aluminum alloy coating shows the oxide coatings to have higher critical loads than the aluminum alloy coatings thus indicating better interfacial strength.

C. *Environmental Exposure Testing and Characterization*

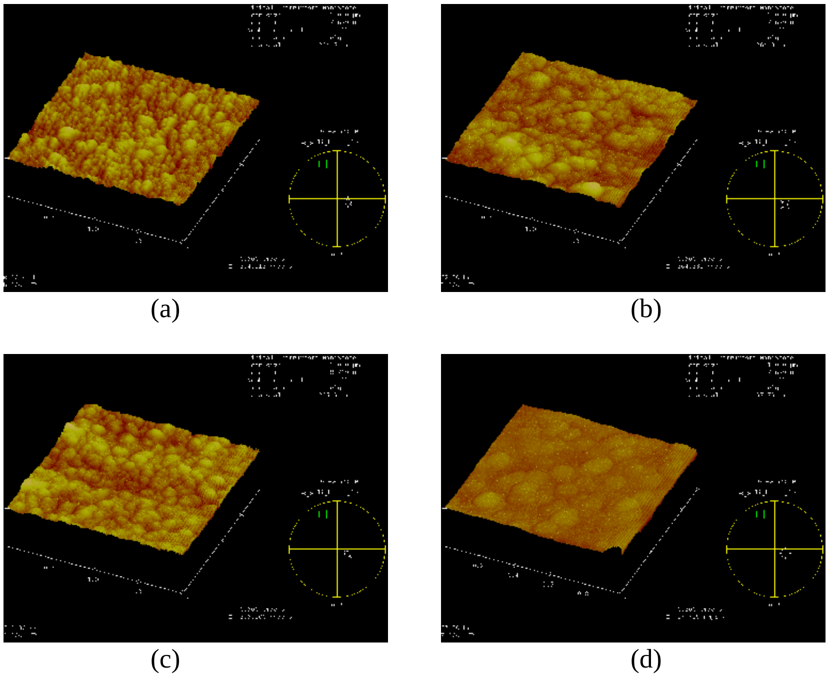
Environmental exposure testing is another critical component to evaluating PLD coating for potential hydrogen and hydrogen isotope applications. In-service operating conditions can result in the exposure of the coatings to not only hydrogen and hydrogen isotopes but also to other potentially deleterious environments such as air and water vapor at elevated temperatures—up to 450-500°C. For this testing representative oxide, carbide, and metallic coatings were exposed to flowing air and a Ar-3H_2 gas mixture at 350°C for up to 100 hours. Following these exposures atomic force microscopy was once again employed to evaluate the microstructural changes of the coating, to check for spalling, delamination, or cracking, and to evaluate the overall surface roughness as a qualitative measure of stability. From these evaluations two preliminary conclusion can be developed: 1) the overall evaluation of the PLD coating technologies potential use, and 2) a qualitative evaluation of the 4 representative coating materials as potential candidate hydrogen/hydrogen isotope permeation barriers.

AFM examination of both the air and Ar-3H_2 mixture—Figure 8 and Figure 9—shows very little change in the coating condition following exposure. No evidence of gross coating failure was detected for any of the coating-substrate systems. Furthermore, no evidence of crack development or localized delamination was detected. The major feature change noted from the AFM examination was related to microstructual evolution of the grain size. For all of the samples evaluated there was a noticeable increase in the average grain size in the coating microstructure. An analysis of this grain growth delta was conducted using the AFM images and a built-in grain size analysis sub-routine in the AFM control software. Figure 10 displays the change in grain size for the 4 coated and 1 un-coated substrate heated at 350°C for 30 hours. In general all the as-deposited coatings were on the order of 5-20 nm in grain size and they all increased in both environments to between 30-50 nm.

A further evaluation of the susceptibility of the PLD coatings and materials to environmental exposure can be achieved by analyzing the coating-substrate system surface topography. This analysis looks at the surface roughness or change in surface roughness as a means of qualitatively assessing changes—coating-substrate alloying/interaction or preferential attack or reaction of localized areas--in the coating-substrate system. Two analysis approaches have been employed to analyze the surface of the coated samples in this research. Additionally, increased surface roughness can be indicative of an increase in the coefficient of friction, which can be important, if wear or fretting is an issue. The first approach relies on standard surface roughness measurements and analyses parameters RMS, R_a, and R_{max}. These parameters are defined as follows:

1. RMS: Root Mean Square average of height deviation taken from a mean data plane
2. R_a: Mean Roughness: Arithmetic average of the absolute values of the surface height deviations measured from the mean plane
3. R_{max}: Max Height: Maximum vertical distance between the highest and lowest data points in the image

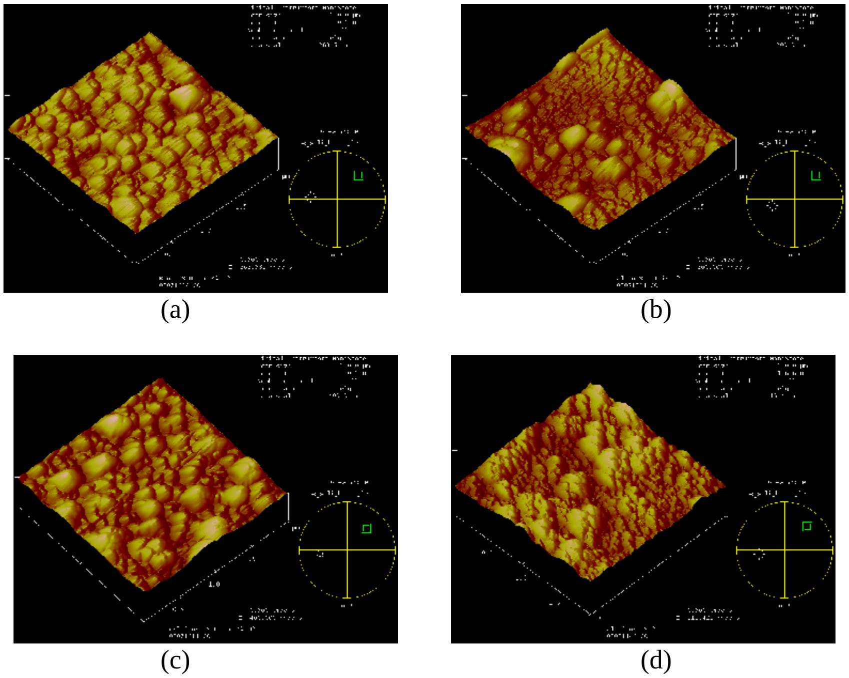
RMS, R_a, and R_{max} were evaluated from the AFM images for the Al, TiC, Cr_2O_3, and Al_2O_3 coatings on a 304L substrate exposed to both air and Ar-3H_2 at 350 °C for 30 hours. This roughness data is shown in Figure 11. Examination of the data in Figure 11 shows in general minimal deviation of the roughness parameters from the baseline measured values. The only notable exceptions are the Al_2O_3 and Cr_2O_3 coatings, which show statistically relevant fluctuations after exposure. These increases in the roughness parameters may be indicative of some micro-fluctuations in oxide stoichiometry/composition or moisture content during testing, however, the majority of the data suggest that there is minimal to no effect on coating stability following the different environmental exposures.



(a) (b)

(c) (d)

Figure 8 Representative AFM Evaluation of Coating-Substrate Systems Exposed in Air at 350˜C for 30 hours: a)Uncoated 304L substrate, b)Al_2O_3 on 304L, c)Cr_2O_3 on 304L, d) Al on 304L—2μ X 2μ scan area.



(a) (b)

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Figure 9 Representative AFM Evaluation of Coating-Substrate Systems Exposed in Ar-3H_2 at 350˜C for 30 hours a)Uncoated 304L substrate, b)Al on 304L, c)Cr_2O_3 on 304L, d)Al_2O_3 on 304L—2μ X 2μ scan area..

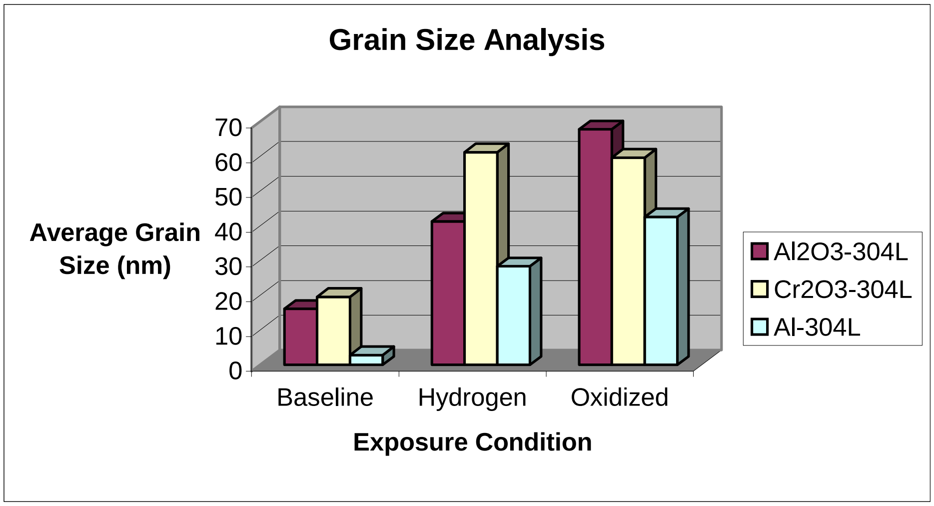


Figure 10 Average Grain Size Evaluation for Coating-Substrate Systems Exposed in both Air and Ar-3H_2 at 350°C for 30 hours.

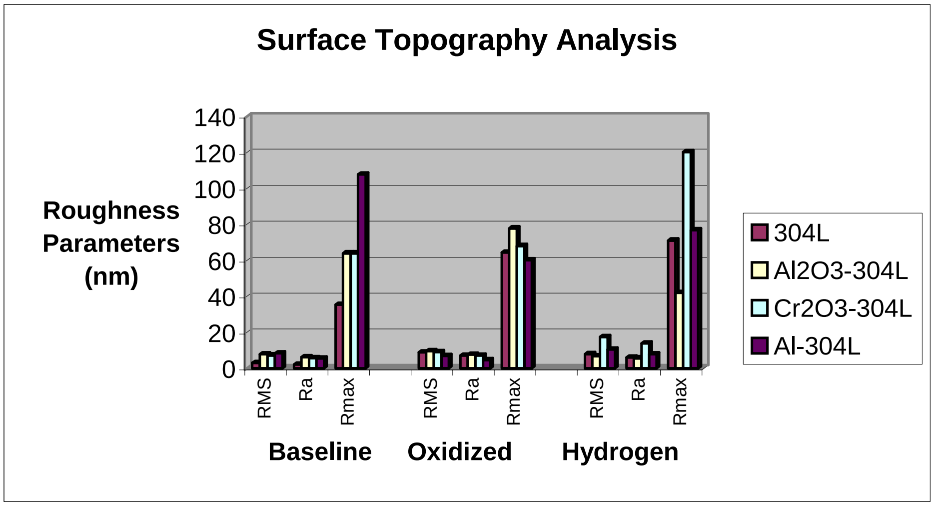
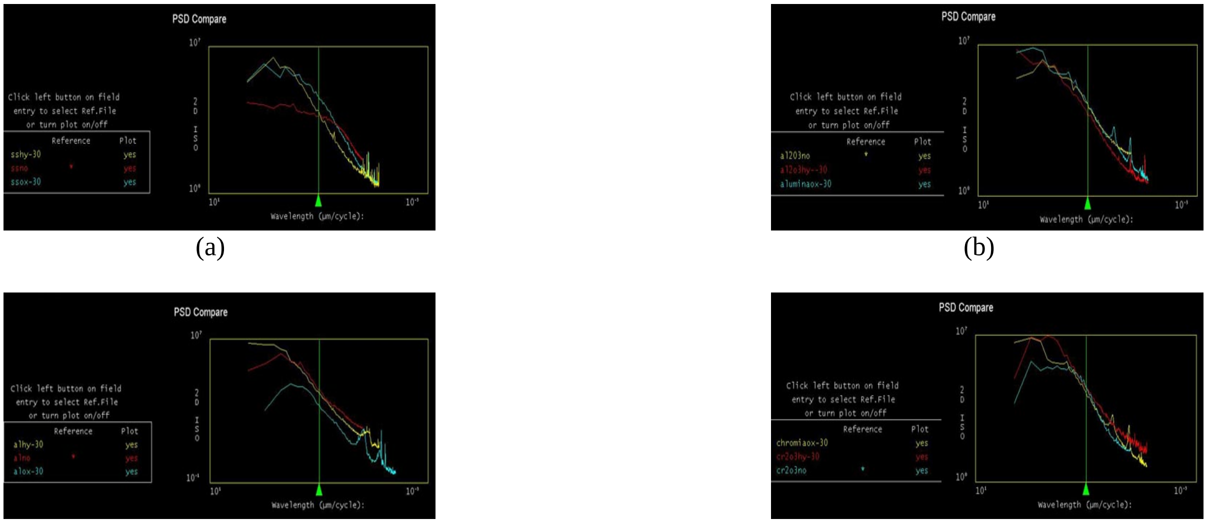


Figure 11 Standard Roughness Analysis RMS, R_a, and R_{max} for Coatings Exposed in both Air and Ar-3H_2 at 350°C for 30 hours

Another analytical approach to evaluate surface topography is by using the power spectral density (PSD) function. This function provides a graphical representation of the amplitude of surface roughness as a function of the spatial frequency of the roughness. The PSD function clearly reveals surface features that might initially appear to be random and graphical displays how these features are distributed over a sample surface. Spikes above background on the PSD plots are characteristic of surface features and define their wavelength spacing. Analysis of the same samples evaluated using the standard surface roughness parameters was performed using the PSD function--Figure 12.



(a) (b)

(c) (d)

Figure 12 Two-Dimensional Power Spectral Density Plots for Coatings Exposed in both Air and Ar-3H_2 at 350°C for 30 hours a)Uncoated 304L substrate, b)Al_2O_3 on 304L, c)Al on 304L, d)Cr_2O_3 on 304L.

Examination of the power spectral density plots in Figure 12 shows the PSD function to be more sensitive than the standard roughness parameter approach. All of the samples show some evidence of roughened features in their PSD plots at both exposure conditions. The intensity of the spikes above background is not large thus indicating small amplitudinal fluctuations, however, these changes appear to be masked or underrepresented by the traditional roughness parameters. Evaluation of the surface using both the traditional roughness and PSD provides a unique, simple approach, however, it is possible that some error can result from surface contamination and vibrational noise distortions.

Summary

A laser-based permeation barrier coating application technology—Pulsed Laser Deposition was evaluated with oxide, carbide, and metal coating systems. The coating materials evaluated are candidate next generation coating materials. This evaluation of the coating application technology and the preliminary evaluation of the candidate coating materials has been achieved using a variety of testing and characterization techniques.

Pulsed laser deposition has bee shown to be an extremely versatile coating deposition technique. This study has demonstrated the capabilities of PLD to apply a wide variety of multicomponent materials using a single set-up.

The as-applied and environmentally exposed coatings have displayed excellent coating adhesion. Characterization of the coating adhesion using AFM has shown no evidence of spalling or cracking. Additional characterization of the microstructural/surface changes of the coating following exposure to both O_2 and H_2 has detected minor changes in grain size and surface roughness the extent of which, however, did not result in delamination or cracking.

All of the candidate coating/substrate systems showed excellent performance under as-applied and simulated service environment conditions. Based on the results for mechanical adhesion and with knowledge of the previously documented permeation effectiveness of the selected test coating materials it is wholly expected that the PLD coatings tested in this study would perform as well or better than the current generation of permeation coatings. Thus, these systems should be further screened for ranking and down-selection for next-generation service.

References

1. J.M. Fitz-Gerald, P. D. Rack, Journal of Applied Physics **86**(3), 1759-1761 (1999).
2. J.M. Fitz-Gerald, T. A. Trottier, Applied Physics Letters **72**(15) (1998).
3. D.B. Chrisey, J. S. Horwitz, Thin Solid Films **206**, 111-115 (1991).
4. Geohegan, D. B. and A. A. Puretzky, Applied Physics Letters **67**(2), 197-199 (1999).
5. D.H. Lowndes, D. B. Geohegan, Science **273,** 898-903 (1996).
6. P R. Willmott, F. Antoni and M. Dobeli, Journal of Applied Physics, 88, 188 (2000).

7. T. Szorenyi, Z. Kantor, Z. Toth and P. Heszler, Applied Surface Science, 139, 275 (1999).
8. F. X. Rong, Applied Physics Letters, 67, 1022 (1995).
9. T. Ishiguro, T. Shoji and H. Inada, Applied Physics A, 69, S149 (1999).