

Program Title: Advanced Nanostructured Hybrid Coatings for the Protection of Aircraft Aluminum Alloys

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Program Summary. Corrosion protection properties of sol-gel-clay-polyelectrolyte coatings are investigated in this project. The inspiration for this anticorrosion coatings are taken from the natural organic-inorganic composite – mother-of-pearl (aka nacre). It reveals numerous unique mechanical properties including, strength, toughness, and wear resistance, which are attributed to the layered structure of the nacre materials (Figure 1). The goal of this project is to create a multifunctional nacre-like coating with excellent mechanical and corrosion resistant properties. The layer-by-layer (LBL) method is used as a primary method of structural design of the coatings and enables combining different functionalities in the multilayer structure. Sol-gel overcoat is used to enhance the barrier and corrosion protection properties of the entire coating.

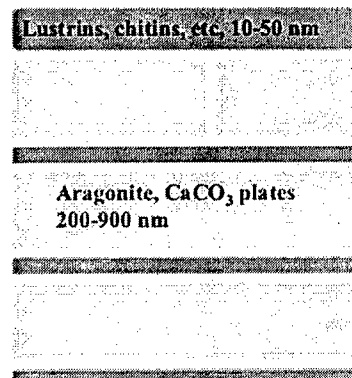
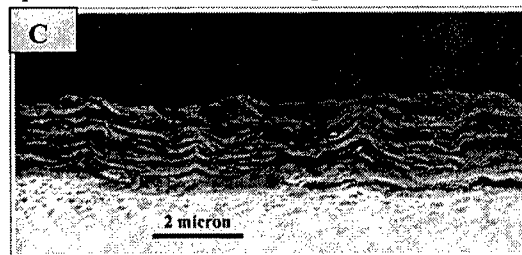
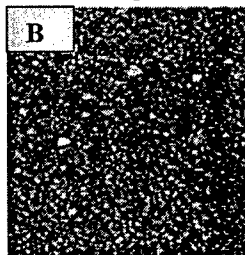
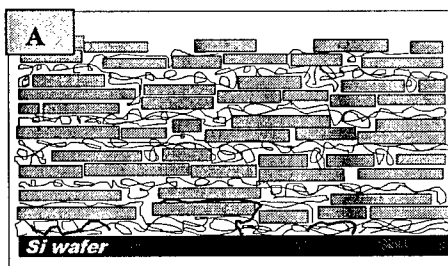


Figure 1. Structural schematics of the mother-of-pearl (nacre).



Optimization of the corrosion protection properties and development of the straightforward protocols for the removal of the coatings are also included in the targets of this research.

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Figure 2. (A) Structural schematics of the clay-PDDA films. (B) AFM image of the clay-PDDA films. (C) SEM image of the cross-section of clay-PDDA films.

Approach.

Structural and Mechanical properties.

Clay-polyelectrolyte multilayers are made on aluminum surface from water-based solutions/dispersion in a simple computer-controlled cyclic procedure. The structure of this primary

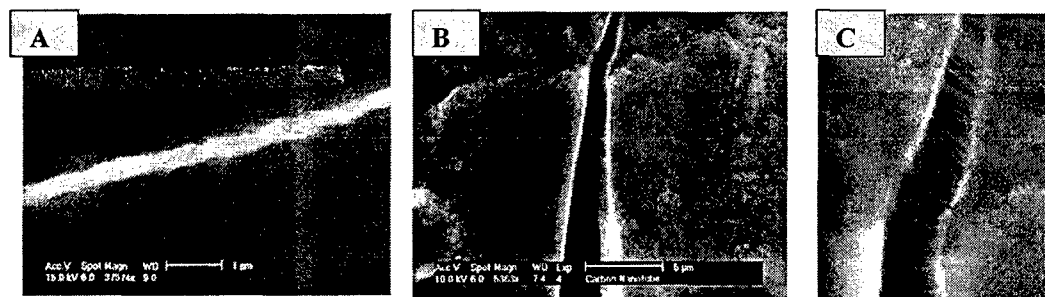


Figure 3. SEM images of SWNT-PVA LBL coating on Al substrate. (A) Cross-sectional image. (B and C) Mechanically stressed areas at different magnifications. Image in (C) demonstrates the presence of large amount of SWNTs in the coatings, strengthening the multilayers.

coating has direct analogy with the structure of nacre (Figure 2A) at many different length scales. Clay platelets are oriented parallel to the surface, which provide barrier function (Figure 2B). The SEM cross-section is clearly reminiscent of the structure of the seashells (Figure 2C). The strength and other mechanical properties of these coatings are very similar to those of the real mother-of-pearl $T=110$ MPa. Further optimization of the preparation procedure allowed us to further increase **strength of the coatings to 400 MPa** by utilizing single-wall carbon nanotubes (SWNTs) (Figure 3). Important to mention that such high strength of the coatings leads to combined with high toughness of these films and wear resistance characteristic for nacre-like materials. The accurate measurements of toughness are now in progress. The morphological features of the SWNT films (Figure 3C), indicate crack resistance of the films is likely to be better than for other aircraft coatings because of bridging of the cracks with SWNTs. High spring constant of the nanotubes can results in closing of the cracks even for very high bending stresses characteristic for wings of aircrafts.

Several other film compositions were tested as well. We have investigated changing the binding polymer to one with much greater strength, such as chitosan. Chitosan/clay forms excellent LBL films although the strength of these films only slightly exceeded those made with PDDA, $T = 130$ MPa.

We have also investigated using a water-based epoxy to improve the binding between layers. According to the advice of our consultant a WPAFB, Janis Brown, we have also tested Epi-Resin and Epi-Kure epoxy components as parts of the LBL coating by dipping. This results in PDDA/clay/epoxy films displayed better visible adhesion than clay-PDDA but corrosion protection with the epoxy films was not competitive with the other formulations possibly because of the chemical reactions between of the epoxy components with Al surface. Additionally epoxy resin LBL films stored only miniscule amounts of corrosion inhibitors (see below).

Graphite coatings have been known for anticorrosion effects. In part this can be attributed to the electrical conductivity of the films. Graphite sheets can be particularly attractive in comparison with SWNT because of high cost of the latter. However, graphite in its native form does not stick to the surfaces very well, particularly the aluminum surface. LBL deposition affords making highly adherent and uniform coatings of graphite sheets. Exfoliated oxidized graphite platelets obtained from Dr. Ruoff were dispersed in water bath with high-power sonicator. Graphite precipitated immediately and no stable dispersion formed. 1-pyrenesulfonic acid can be used as a dispersing agent. This chemical is well known for its ability to disperse carbon nanotubes and graphite platelets in polar solvents. Dispersing the graphite sheets in ethanol led to solutions which could be used to make LBL films by immersion. PDDA and poly(vinyl alcohol), PVA, were used as counter ions. Ultraviolet-visible absorption spectra of films formed on glass slides show an increase in absorption as the number of layers increase (Figure 4A). The films, however, are not uniform, because the graphite platelets are still agglomerated, and large clumps adsorb to the surface as evidenced by optical microscopy (Figure 4C).

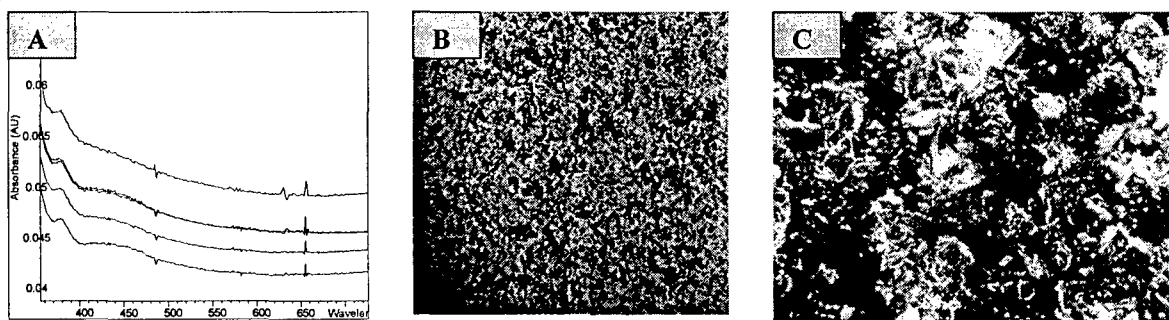


Figure 4. (A) UV-vis monitoring of the LBL assembly of graphite platelets. (B and C) Optical micrographs of the graphite platelets LBL layer coatings.

Anticorrosion properties.

These primary LBL coatings are infused with active corrosion inhibitor, which can be stored between the layers. We tested several potential inhibitors which include Cr(6+), Cr(3+), Co(3+), Ce(4+), oxalic acid, tobacco extract (did not exhibit noticeable corrosion protection) and dispersion of polyaniline. Cerium-infused samples demonstrated the best results so far. It needs to be noted that after the LBL deposition and inhibitor infiltration the surface is sprayed with a sol-gel, which partially penetrates in the LBL film. The obtained films have stratified structure, which makes possible corrosion prevention by two mechanisms. The LBL-sol-gel mixed stratum works as an barrier film better than LBL or sol-gel coatings separately. At the same time, the barrier characteristics of the coating do not conflict with (rapid) diffusion of an active corrosion inhibitor along the clay layers. The corrosion inhibitor can be delivered to the defect sites (scratches, nicks, etc.) and suppress the corrosion process.

The batches of salt fog samples were tested according to ASTM B-117 for 168 hours. As a control, samples with ORMOSIL sprayed directly on desmuted aluminum that had been soaked for 30 minutes in cerium acetate solution were used. All the other samples were on desmuted aluminum and had mixed layers sprayed on them. First, five bilayers of (PDDA/PAA) were applied (and samples dried for a few hours or even overnight) and then (PDDA/clay/PDDA/PAA) was applied for 3, 6, or 2.5 layers. The 2.5 layers sample was done so that some samples would finish with PAA and some with clay. Half of the samples were then treated with Co solution while the other half was soaked in cerium acetate. The following table and the legend provides the detailed information on these samples.

Table 1.

Sample	Salt fog	Adhesion (psi)	Rcorr (PDS) k . cm ²	Epit (PDS) V	Rcoat (EIS) k . cm ²	Ycoat (EIS) nF/cm ²	Ccoat (EIS) nF/cm ²
A	1	270 ± 219	792	3.35	256	8.1	9.9
B	4	225 ± 40	803	0.48	82	76.5	55.0
C	4	433 ± 272	1423	2.32	271	8.0	10.1
D	2	465 ± 532	1065	2.29	215	85.8	41.2
OM	5	750 ± 447	2446	2.75	102		13.4

OMCo	5	1370 ± 700	808	2.4	130		24.2
A2	2	1080 ± 550	2750	1.99	30	25.3	19.6
B2	1	1750 ± 300	440	1.46	18	16.0	16.0
C2	3	920 ± 240	845	1.67	280	53.3	29.6
D2	3	1450 ± 260	730	0.44	12	25.3	13.7
1-1 to 1-3	4	1010 ± 100	508	1.95	78		11.6
2-1 to 2-3	4	720 ± 330	641	2.24	19	7.8	11.9
3-1 to 3-3	3	700 ± 260	607	1.88	21		14.8
1-4 to 1-6	4		1726	3.44	477	9.1	9.2
2-4 to 2-6	5		1601	2.93	155		9.1
3-4 to 3-6	4						
4-1 to 4-3	5		2193	2.09	141		21.3

Sample description:

OM = ORMOSIL sprayed directly on desmuted aluminum

A1 = PEI/PAA/PEI/clay & Co solution & ORMOSIL on desmuted aluminum

B1 = PDDA/PAA/PDDA/clay & Co solution & ORMOSIL on deoxidized aluminum

C1 = PDDA/PAA/PDDA/clay & Co solution & ORMOSIL on desmuted aluminum

D1 = PEI/PAA/PEI/clay & Co solution & ORMOSIL on deoxidized aluminum

OMCo - ORMOSIL sprayed directly on desmuted aluminum that was soaked in Co solution

A2 - PEI/PAA & ORMOSIL on desmuted aluminum

B2 - PDDA/PAA & ORMOSIL on desmuted aluminum

C2 - PEI/PAA & Co solution & ORMOSIL on desmuted aluminum

D2 - PDDA/PAA & Co solution & ORMOSIL on desmuted aluminum

1-1 to 1-3 – (PDDA/PAA)5(PDDA/clay/PDDA/PAA)3 & Co solution & ORMOSIL on desmuted aluminum

2-1 to 2-3 – (PDDA/PAA)5(PDDA/clay/PDDA/PAA)6 & Co solution & ORMOSIL on desmuted aluminum

3-1 to 3-3 – (PDDA/PAA)5(PDDA/clay/PDDA/PAA)2.5 & Co solution & ORMOSIL on desmuted aluminum

1-4 to 1-6 – (PDDA/PAA)5(PDDA/clay/PDDA/PAA)3 & cerium acetate & ORMOSIL on desmuted aluminum

2-4 to 2-6 – (PDDA/PAA)5(PDDA/clay/PDDA/PAA)6 & cerium acetate & ORMOSIL on desmuted aluminum

3-4 to 3-6 – (PDDA/PAA)5(PDDA/clay/PDDA/PAA)2.5 & cerium acetate & ORMOSIL on desmuted aluminum

4-1 to 4-4 - ORMOSIL sprayed directly on desmuted aluminum that was soaked in cerium acetate

Figure 5 provide the visual images of the corrosion protection **after the salt fog chamber experiment**. As one can see, the engineered coating provides very good protection of Al surface (Samples 2-4, 2-6). Comparison of the 1-3 with 1-5 indicates that indeed Ce-infused samples

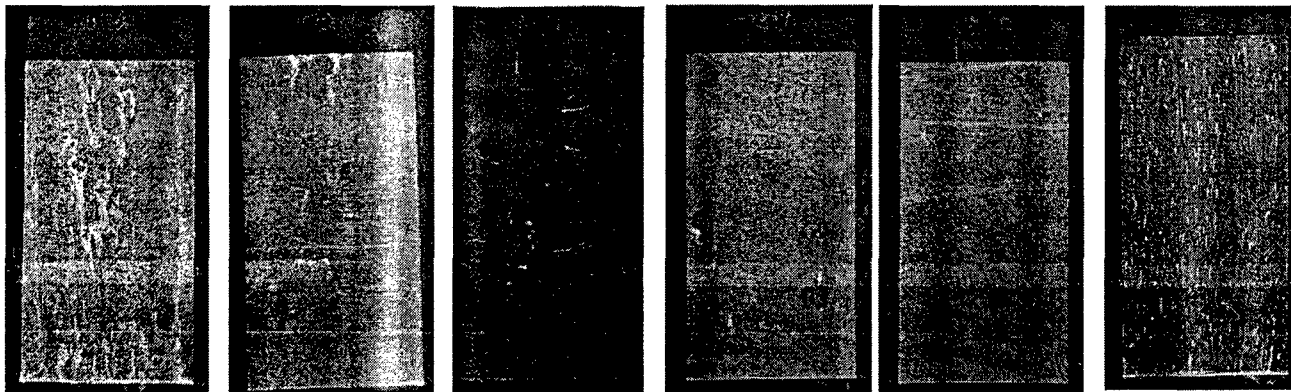


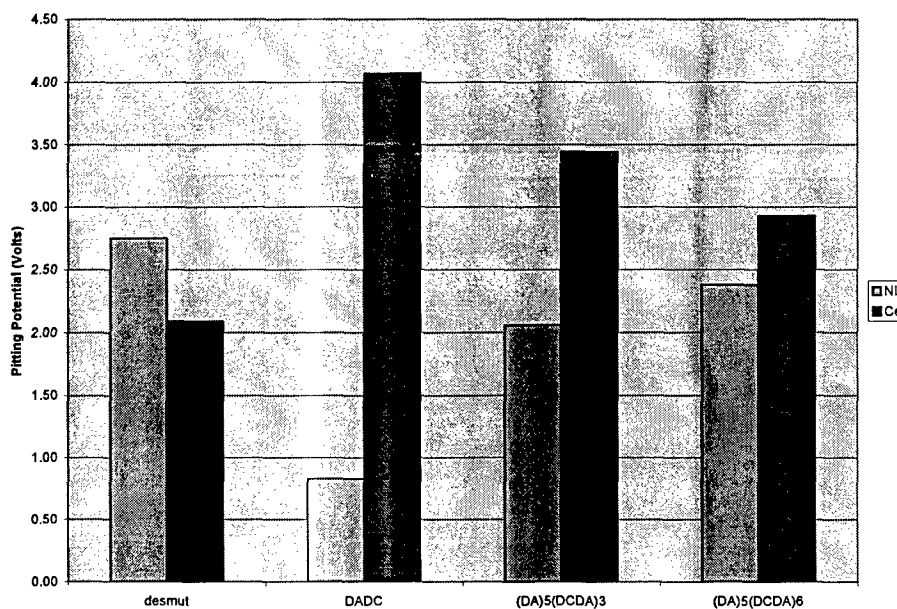
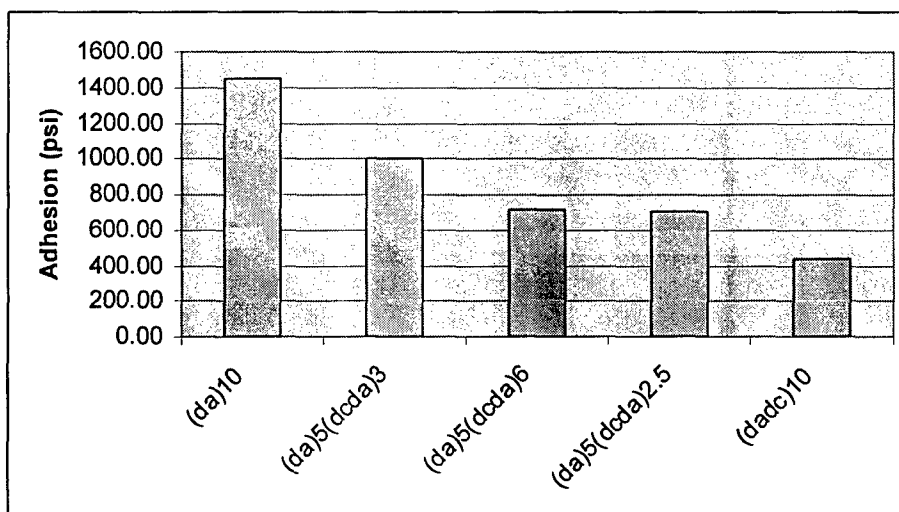
Figure 5. Optical photographs of Al samples after salt fog chamber tests. Sample number is given on the images. The description of the samples is given in Table 1.

provide much better protection than Co-infused multilayers.

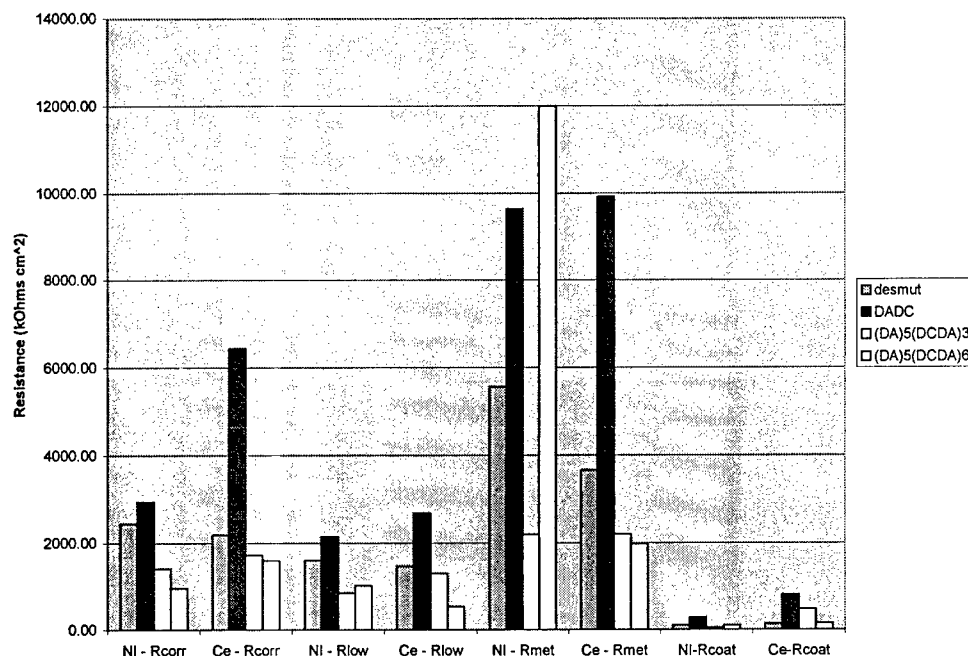
Important to note that (compare sample 4-2 vs. samples 1-5, 1-6, 2-4, 2-6) these experiments clearly indicates that the **addition of LBL films results in a better corrosion protection than just the ORMOSIL layers alone**. This point is being verified now by the investigation of Ce diffusion in the LBL films. Ongoing experiments are aimed at the demonstration of the redistribution of Ce in the films after scratching the surface. As well the corresponding diffusion modeling simulation experiment is being developed. The program will allow us to predict the corrosion inhibition efficiency of the future films without the need for time consuming salt-fog experiments.

One of the important issues that we are currently working on is the improvement of the adhesion of the multilayer films to the substrate. The adhesion values for the mixed layers fall in between those of polyelectrolyte only and those with clay from the first layers. The adhesion drops when more clay layers are used or when the LBL stack finishes with clay rather than with PAA. Although the best adhesion results for the multilayer films exceed desirable the minimum adhesion parameters specified for aircraft coatings

This indicate that The standard deviations range from 100 to 330 psi, so there is some overlap between the measurements. Note that all of these samples had been treated with cobalt solution and then had ORMOSIL applied. We will be doing some adhesion testing with cerium acetate-treated samples.



First, it is clear that soaking the LBL layers in cerium acetate prior to ORMOSIL coating improves the pitting potential. It is somewhat odd that the improvement is so much greater for the (DADC)10 sample than for the hybrid samples.



For the resistance values, Rcorr is the corrosion resistance from PDS measurements, Rlow is the impedance magnitude at 10 mHz from EIS measurements, and Rmet and Rcoat are calculated from the fit to the impedance measurements. Again the sample with (DADC)10 shows higher values than the other samples.

C is the capacitance calculated from the slope of the high frequency EIS data. Ycoat and Ymet are determined as fitting parameters for the EIS data. In general, a smaller capacitance means a thicker film. C and Ycoat are measured in nF/cm² and nS/cm² respectively. Ymet is measured in microS/cm².

Funding Profile:

FY99	FY01	FY02	FY03	FY04	FY05	FY06
0K	0K	152K	132K	146K	0K	0K

Objectives

The following objectives were put forward in the proposal.

1. To understand the chemical and physical processes enabling the corrosion protection in hybrid coatings.
2. To establish structure-property correlations for corrosion protection of these coatings and the nature of nanostructures they are based upon.
3. To develop hybrid coating chemistries optimized to facilitate release of sequestered corrosion inhibitors under conditions associated with the onset of corrosion of AA substrates.
4. To investigate the mechanism of corrosion protection and migration of inhibitor ions through the multilayer LBL/Sol-Gel system.

These objectives can be considered as milestones to the achievement of the more general goals which include:

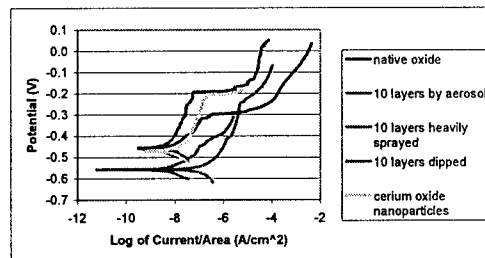
1. Development of ecologically benign corrosion protection and replacement of chromate technologies
2. Development of new corrosion protection materials with broad range of functions.

Status of Effort.

The project is successfully completed. The new method of Al protection was developed.

Currently we transferred this technology to our industrial partners who are working with Tinker AFB to reduce is to practice.

1. Stratified systems comprising an inhibitor-doped layer-by-layer (LBL) clay-polyelectrolyte overcoated with a dense organically-modified silicate (Ormosil) are investigated as corrosion protectors for aluminum. As separate coatings, neither the LBL nor Ormosil films were found to provide adequate corrosion protection of the underlying metal. A combination of the two coating methods was found to produce a synergistic enhancement of corrosion resistance characteristics, as determined by using electrochemical techniques. This effect occurs due to the formation of sol-gel cross-linked LBL multilayers. Moreover, the LBL-sol-gel hybrid stratum seals the inhibitor ions into the polyelectrolyte layer, thereby producing a reservoir of corrosion inhibitors in the direct vicinity of the metal. Importantly, the LBL multilayers not affected by sol-gel promote lateral diffusion of an active corrosion inhibitor along the surface. Such a layered system can be considered as an example of performance optimization by multilayer stratification of nanostructured materials.



2. Corrosion processes on aluminum were investigated with different techniques, which include Electrochemical Impedance Spectroscopy (EIS) (Figure 3), scanning electron microscopy, transmission electron microscopy, and atomic force microscopy. Recently a new technique was introduced as a tool for the investigation of the corrosion processes. This is confocal microscopy the nanoparticle labels. This method is based on the decrease of the nanoparticle luminescence in response to pH drastically changing in the corroded areas.

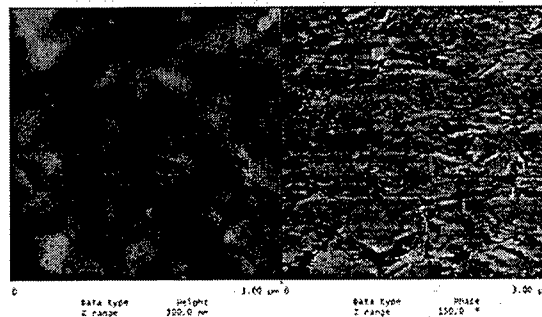


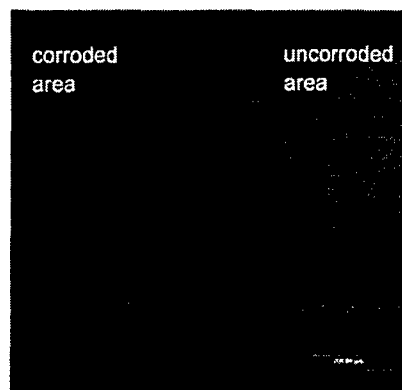
Figure 3 Atomic force microscopy image of film sprayed with 3 layers of (PDDA/clay) on a mica sheet. The height image (left) suggests that some of the clay platelets may be tilted or even perpendicular to the substrate rather than parallel. The phase contrast image of the same region is shown on the right. Both images are of a region 3 micrometers across (collaboration with Nomadics Inc).

3. The structure-property correlation between EIS data, optical microscopy and other techniques with the performance of the films are being investigated. The films were made with and without sol-gel layer by dip coating and by spraying (Figure 2). Different nanostructures are included in the Aluminum coatings such as Cr_2O_3 , CeO_2 and others. Different types of Ormosil top layers are also tested. Examples include Ormosils with CeO_2 components imbedded in the structure.
4. Computer modeling of the corrosion processes is being undertaken. A 2D model of the diffusion in the layered structure resembling LBL films have been developed. The computer model predictions are now being correlated with the experimental results.
5. The mechanical properties of the clay-polyelectrolyte layers are being investigated. The data obtained so far indicate that they can be exceptionally tough and strong. The strength of the polyelectrolyte films increases with the contents of inorganic materials and depends on the orientation of the clay platelets.

Accomplishments

1. The corrosion resistance of the combined composite LBL-Ormosil films is approaching that of chromate coatings. Both coatings separately have insufficient protection. The synergistic effect is related to the combination of the freedom of the corrosion inhibitor diffusion in the vicinity of the Al layer and the strong barrier function. The diffusion layer of the corrosion inhibitor is thin enough not to affect the mechanical properties of the films.
2. The nanoscale diffusion layer in the vicinity of Al surface can also be used as a "parachute" layer to quickly and safely remove the top coating. "Removal-on-command" function was achieved by using citrate solution as well as other cleaning mixtures.
3. The mechanical properties of the clay polymer layer were determined to be exceptionally high. As related to protective coatings, they found to be as tough as nacre (lining material of the seashells). This will ensure their durability on the aircrafts.

4. A new type of microscopy, i.e. confocal microscopy (Figure 4) was used in the practice of corrosion assessment. This was made possible by the utilization of luminescent nanoparticles whose luminescence is strongly dependent on the local pH. Now the corrosion process can be observed in situ at the level of details of several microns
5. A new type of nanoparticles, i.e. CeO_2 nanoparticles was utilized in the corrosion protection of Aluminum. The results obtained after replacement chromium related species with CeO_2 showed improved E_{corr} , E_{pit} , and R_{corr} .



Personnel Supported

At Oklahoma State University, Mr. John W. Ostrander, Mr. Birol Ozturk, Mr. Volcan Cicek, Dr. Yuanfang Liu, Dr. Alex Syniaguin, Dr. Zhiyong Tang, and Dr. Nicholas A. Kotov have been associated. A part of this research was also supported by NSF grant and OCAST grant.

Figure 4. Exemplary confocal microscopy image of Al surface coated with CdTe nanoparticles with red luminescence. The luminescence decreases greatly after corrosion.

Publications

During the last year, several publications were published or accepted based on the Phase I work.

1. Synergistic Corrosion Protection with LBL/ORMOSIL Smart Composite Coatings, O. Kachurina, T. L. Metroke, J. W. Ostrander, E. Knobbe, and N. A. Kotov, *International Journal of Nanotechnology*, **2004**, 1(3), 347-365.
2. Technique for the removal of organic-inorganic hybrid coatings from 2024-T3 aluminum alloy, Olga Kachurina, Tammy L. Metroke and Edward T. Knobbe *Progress in Organic Coatings*, Volume 47, Issue 1, July 2003, 55-60.
3. Enhancement of corrosion resistance characteristics of 2024-T3 aluminum alloy through laser-induced surface modification, O. Kachurina, T. Metroke, K. Dou, accepted by *Journal of Laser Applications*.

Interactions/Transitions

The team has effective collaboration with Nomadics, Inc. (Westcott, Mamedov, Wang, Strecker) and Sciperio Inc. (Kachurina, Knobbe)

Discoveries, Inventions, and Patents

- 1) Knobbe, Edward T.; Kachurina, Olga; Metroke, Tammy L. "Removal of ORMOSIL films from metal substrates" was converted to utility application 10/238,028 from provisional application 60/318,051 on September 9, 2002. Published as United States Patent Application 20030049382 on March 13, 2003. Assigned to Oklahoma State University.
- 2) Knobbe, Edward T.; Kachurina, Olga; Metroke, Tammy L. "Removal of Organically Modified Silicate Films from Metal Substrates" was submitted internationally as application PCT/US02/28562 on September 9, 2002. Assigned to Oklahoma State University.
- 3) Knobbe, Edward T.; *Kachurina*, Olga;; Metroke, Tammy L. "Advanced composite ormosil coatings" Published as United States Patent Application 20030012971 on January 16, 2003. Assigned to Oklahoma State University.
- 4) Parkhill, Robert L.; Knobbe, Edward T.; Metroke, Tammy L.; Kotov, Nicholas; Kachurina, Olga "Integrated Coating System with Release on Command Concepts" was submitted as provisional application 60/347,526 on January 11, 2002 and filed as utility application 10/341,541 on January 13, 2003. Jointly assigned to Oklahoma State University and Sciperio, Inc.
- 5) Kotov, Nicholas; Knobbe, Edward T; Kachurina , Olga; Metroke, Tammy L. "Organic/inorganic multilayer coating system" Published as United States Patent Application 20030027011 on February 6, 2003. Assigned to Oklahoma State University.

Honors/Awards

Invited presentations at

1. Texas A&M University,
2. University of Maryland
3. Gordon Research Conference in Il Ciocco (Italy)
4. Gordon Research Conference in New London (Connecticut)

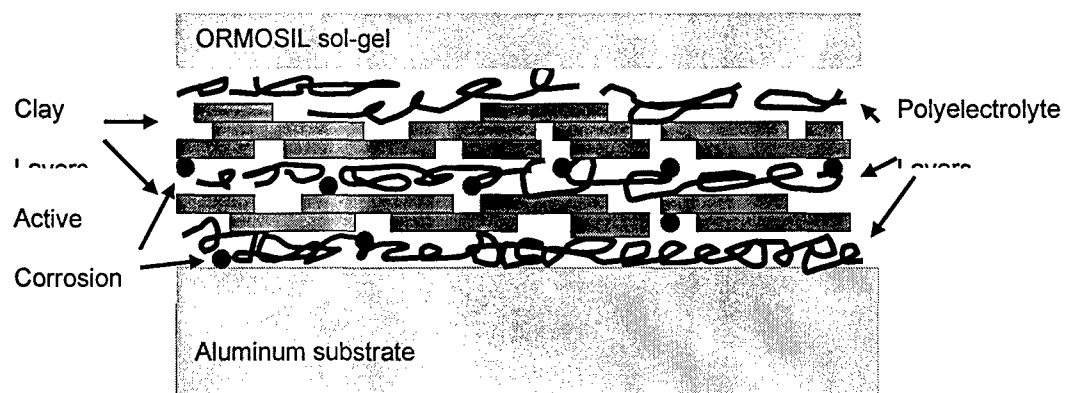
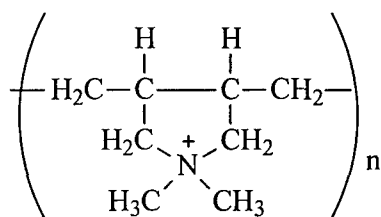
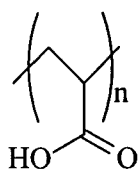


Figure 1 Layers of clay platelets, polyelectrolytes, and active corrosion inhibitors are assembled on the aluminum substrate and coated with an ORMOSIL sol-gel.



PDDA



PAA

Figure 3 The structure of the polyelectrolytes used in the LBL assembly.

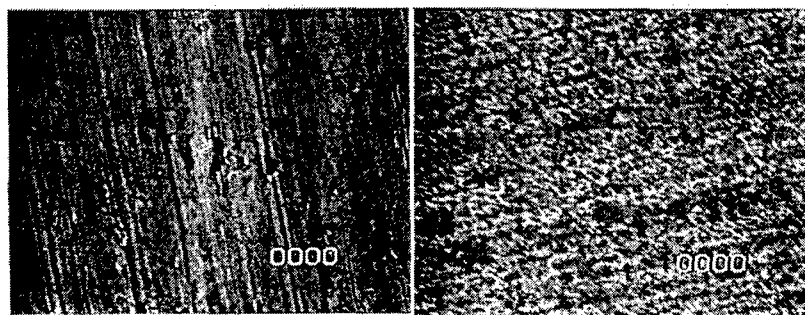


Figure 2 Optical microscope images with 500x magnification of a degreased aluminum surface (left) and a degreased aluminum surface that has been sprayed with 15 layers of PDDA and clay (right).

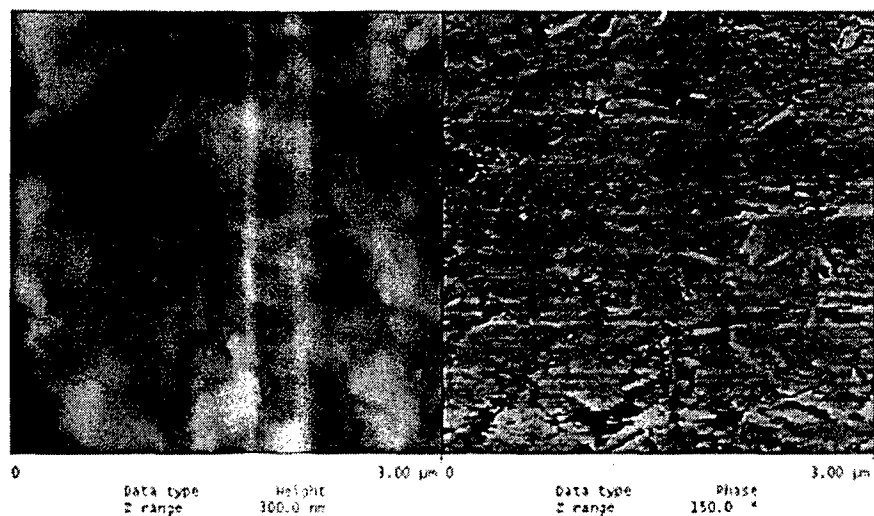


Figure 4 Atomic force microscopy image of film sprayed with 3 layers of (PDDA/clay) on a mica sheet. The height image (left) suggests that some of the clay platelets may be tilted or even perpendicular to the substrate rather than parallel. The phase contrast image of the same region is shown on the right. Both images are of a region 3 micrometers across.

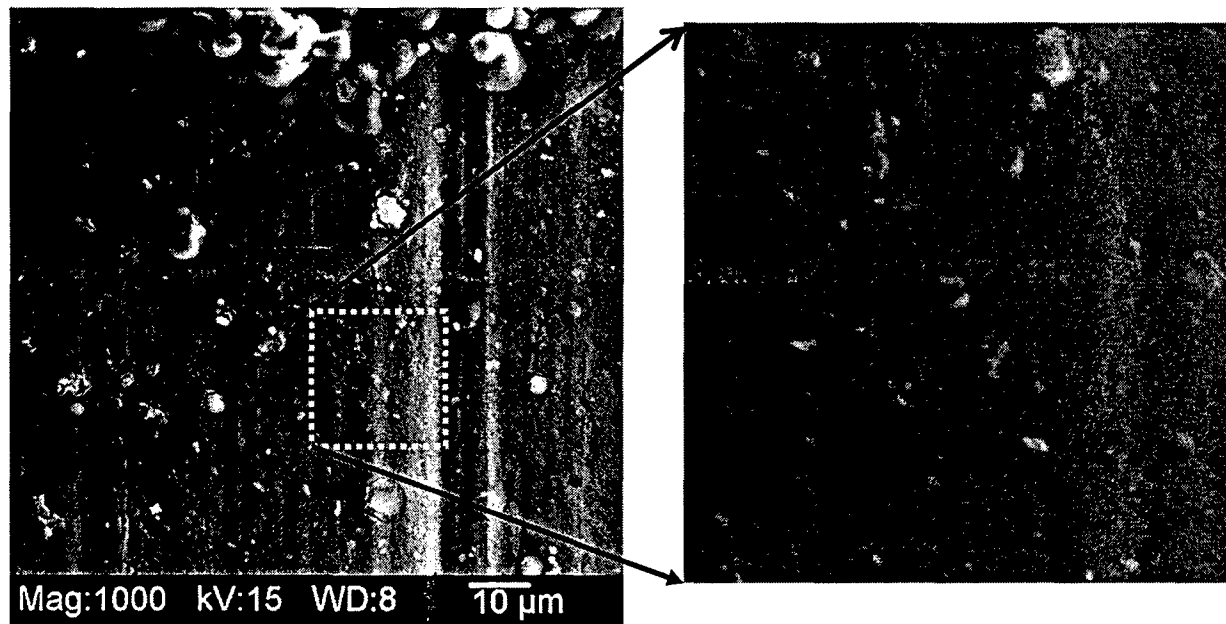


Figure 5 SEM image of one spraying application of PDDA and clay to a deoxidized aluminum substrate. The irregularly shaped white pieces in the blown-up image are the clay platelets. However, the main image is dominated by debris on the aluminum surface; the pits and some of the debris may have been left from the deoxidation process.

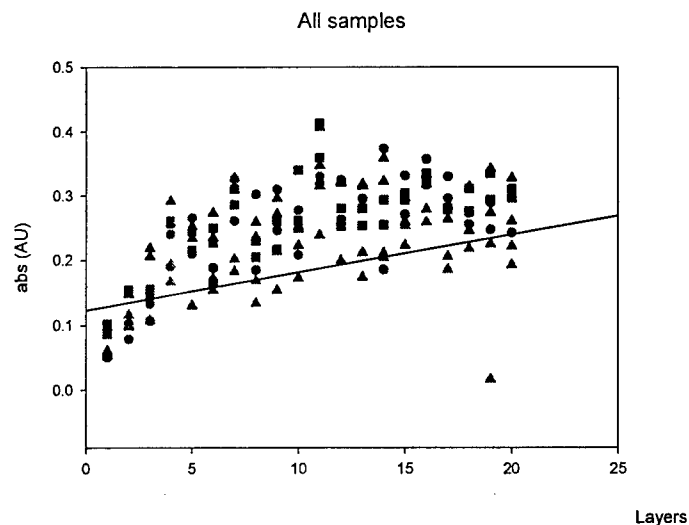


Figure 6 The UV-visible absorbance of typical $(\text{PDDA}/\text{clay})_n$ films on glass slides prepared by aerosol showed an initial linear increase, followed by leveling off.

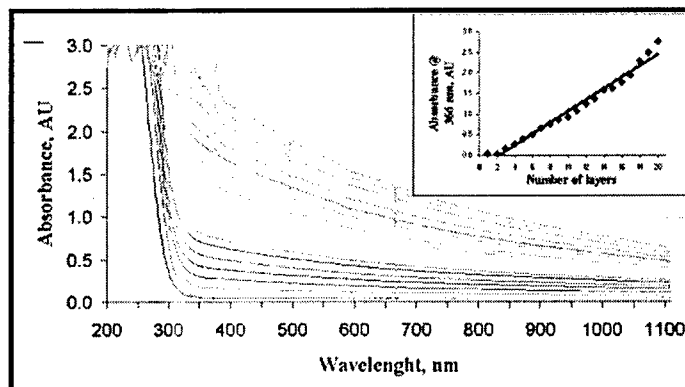


Figure 7 UV-vis absorbance of a glass slide sprayed with bilayers of PDDA and concentrated clay solution. The inset shows how the absorbance at 366 nm increases linearly with the number of bilayers.

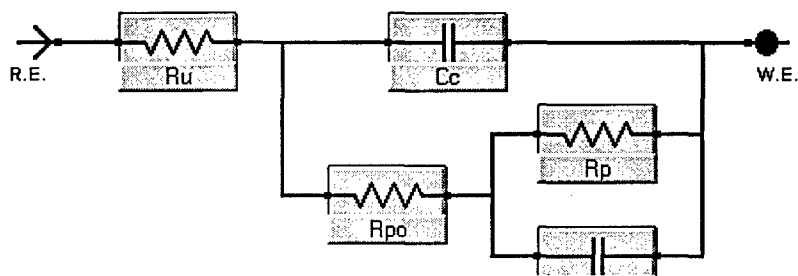


Figure 8 Typical model for coated metal samples used to fit the EIS data. R_u denotes solution resistance, C_c denotes coating capacitance, R_{po} denotes pore resistance, R_p denotes polarization resistance, and C_{dl} denotes double layer capacitance.

Figure 9 PDS data measured for the native oxide of a cleaned aluminum sample, a sample sprayed with 10 layers of (PDDA/clay), a sample more heavily sprayed with the same 10 layers, a sample with 10 layers of (PDDA/PAA/PDDA/clay) prepared by immersion, and a sample prepared by immersion with layers of CeO_2 nanoparticles and PAA.

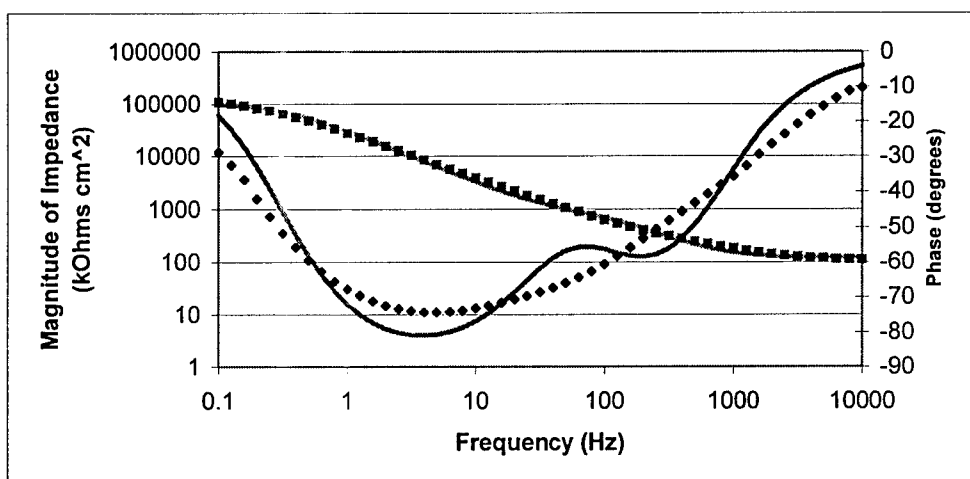


Figure 10 EIS spectra measured for an aluminum sample coated with PDDA/PAA/(PDDA/clay)₁₀ layers by aerosol.

REPORT DOCUMENTATION PAGE

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Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

1. REPORT DATE (DD-MM-YYYY) Oct 3 2005		2. REPORT TYPE Final		3. DATES COVERED (From - To) 5/01/2002-5/31/2005	
4. TITLE AND SUBTITLE Advanced Nanostructured Hybrid Coatings for the Protection of				5a. CONTRACT NUMBER F49620-02-1-0279	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) N. Kotov				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Oklahoma State University Department of Chemistry Stillwater OK 74078				8. PERFORMING ORGANIZATION REPORT NUMBER Oklahoma State University	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) DEPSCoR AFOSR, Jennifer NL				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION / AVAILABILITY STATEMENT Approve for Public Release: Distribution Unlimited					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT The US Air Force is presently facing a critical need to develop environmentally-compliant surface treatments designed to mitigate corrosion of aircraft aluminum alloys (AAs). Currently available surface pretreatments for AAs have been determined to comprise human and environmental health hazards (e.g., hexavalent chromate-based conversion coatings) and/or exhibit limited effectiveness as corrosion inhibitors. The proposed project seeks to leverage DEPSCoR funding aimed at the preparation and evaluation of advanced hybrid coatings that are (1) environmentally-compliant, (2) serve as an effective barrier layer and are readily incorporated into a multilayer paint system, and (3) contain a reservoir of nanoengineered structures targeted to provide electrochemically-active corrosion inhibitors "on demand" in the case of a barrier layer breach. In the event of a mechanical breach of a simple hybrid barrier layer, however, corrosion can proceed due to the absence of effective corrosion-inhibitor incorporation. Attempts to add soluble corrosion inhibitors to prepared organic-inorganic layers have shown limited effectiveness, due to slow migration kinetics of entrapped inhibitor species through the dense barrier layer. The proposed work seeks to incorporate newly developed nanotechnologies					
15. SUBJECT TERMS Corrosion, nanomaterials, clay, composites, sol-gel					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER (include area code) 734-763-8768