Development and Evaluation of Nanostructured Coatings for Coal-Fired Environments

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Presentation Outline

- Introduction
- Background
- Nanocoatings
- Experimental Details
- Coating evaluation
- Conclusions

Introduction

- Stricter regulatory conditions requiring a reduction in CO_2 emissions are forcing utilities to improve the efficiency of power generation technology to operate at 50-55%.
- Efficiency of conventional fossil power plants is strongly related to operating temperatures and pressures.
- Material choices and material issues vary for subcritical (1950s) and supercritical (1960's) power plants
  - *Subcritical* : Less than 22 MPa (~3200 psi pressure) and had efficiencies in the range of a 35 to 37% high heating value (HHV).
  - *Supercritical* : 563°C (1050°F) and pressures of 25 MPa (3600 psi).
  - *Ultra-supercritical (USC)* : Plans to achieve steam conditions with temperatures of 760°C (1400°F) and pressures of 35 MPa (5000 psi)

Introduction

- Power plants incorporating USC technology can achieve higher cycle efficiency, and lower emissions of sulfur dioxide, oxides of nitrogen, and carbon dioxide than current coal-fired power plants.
- However, the materials and coatings that are used in current boilers do not have the high-temperature strength and corrosion resistance required for USC operation.
- The increase in steam temperatures, which could enhance the efficiency in power generating systems, could result in further increase in corrosion rates.

Need for Advanced Materials

- Oxidation resistance in these advanced materials such as ferritic and austenitic alloys is attributed to the formation of Cr-containing oxides. However, these oxide layers are known to become less protective at higher temperatures and in steam or exhaust environments.
- Hence, a major concern in using advanced materials systems such as Fe- and Ni-base alloys at such higher temperatures in fossil energy system environments, where sulfur and water vapor are present, is their poor oxidation and corrosion resistance .

Surface Coatings

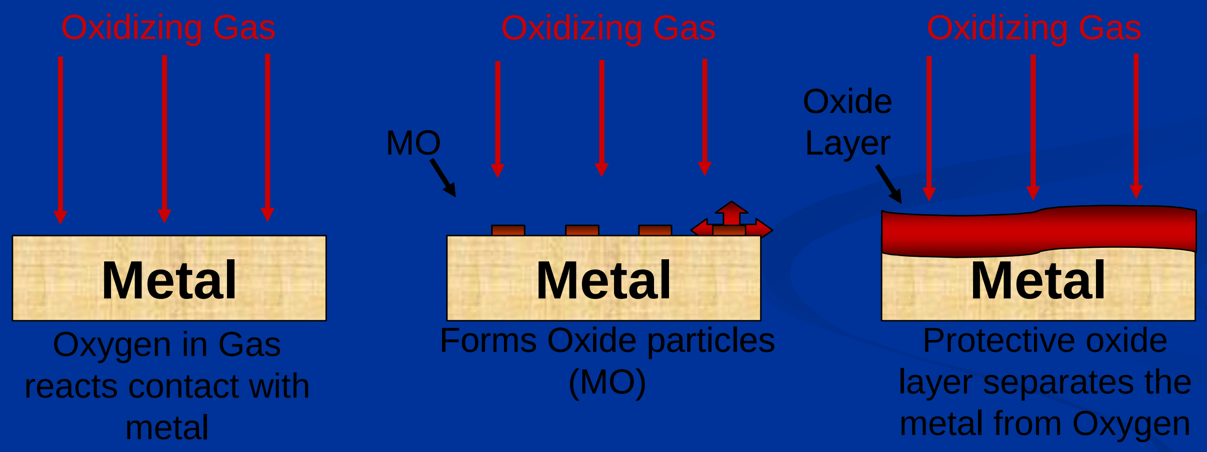
- Corrosion performance of power plant components can be improved by the use of advanced coatings.

- The protective coatings that are developed should be optimally designed as part of the overall power generation system, should be easily maintainable, and should be capable of non-intrusive evaluation to determine remaining life.

Use of coatings

Oxide Layer Provides Oxidation/Corrosion Protection

Metal (S) + ½ Oxygen (g) = Metal Oxide (S)



Minimum Al or Cr concentration required to form a continuous oxide layer:

- For Alumina scale formation: 5-6% Al
- For Chromia scale formation: 20-25% Cr

Conventional Coatings

- Require high Cr levels in the weld overlays and coatings for tube protection (high Cr lowers wastage rate)
- High Cr containing overlays/Fe-Cr coatings are susceptible to in-service embrittlement
- Circumferential cracking in weld overlays is the primary failure mode (takes about 2 to 6 years) – thickness, residual stresses and thermal fatigue - responsible for cracking
- Thermal spray coatings exhibited short life (1 to 3 yrs) – poor quality of the coating and improper surface preparation leading to coating spallation
- Diffusion coatings performed poorly – variation of Cr or Al content is partly responsible

Nanostructured coatings

New type of coating systems are needed with increasing demand for enhancing the efficiency, performance, cost, and extended coating life.

- **Single or multi-phase polycrystalline solids**
- **Typical grain sizes are less than 100 nm (1 nm = 10^{-9} m = 10Å)**
- **A distinct characteristic of nanocoatings is the presence of a large number of grain boundary interfaces**
- **Offer excellent corrosion/oxidation/erosion properties compared to conventional materials/coatings**

*C. Suryanarayana and Koch, Hyperfine Interactions, 2000, 130, 5-44.

Coating Process

- Plasma-Enhanced, Magnetron Sputtering (PEMS) process developed by Southwest Research Institute (SwRI) was used for depositing nanostructured coatings.
- Technology was based on magnetron sputter deposition, a physical vapor deposition (PVD) process.
  - Differs from conventional PVD processes in that it consists of a hot-filament generated plasma to achieve the plasma enhancement.
  - Increases coating density and reduces the grain size of coatings to a few tens of nanometers.

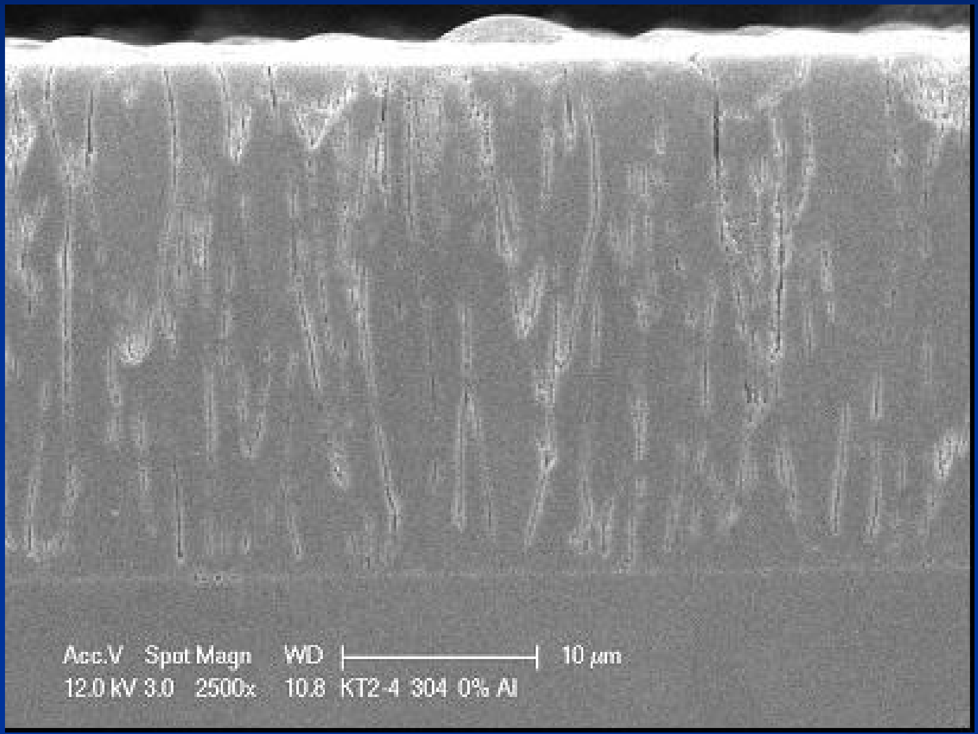
Coating Systems

Substrate	Typical Substrate Composition	Typical Coating composition
304L	Fe-18Cr-8 Ni	304 + 0% Al 304 + 4% Al 304 + 10% Al
P91	Fe-9Cr-1Mo-0.55Mn-0.40Si-0.22V-0.36Ni-0.10C	Ni-20Cr-4% Al Ni-20Cr-7% Al Ni-20Cr-10% Al 304 + 4% Al 304 + 10% Al
Haynes 230	57 Ni-22Cr-14W-2Mo	Ni-20Cr-4%Al Ni-20Cr-7%Al Ni-20Cr-10%Al

Coating Evaluation

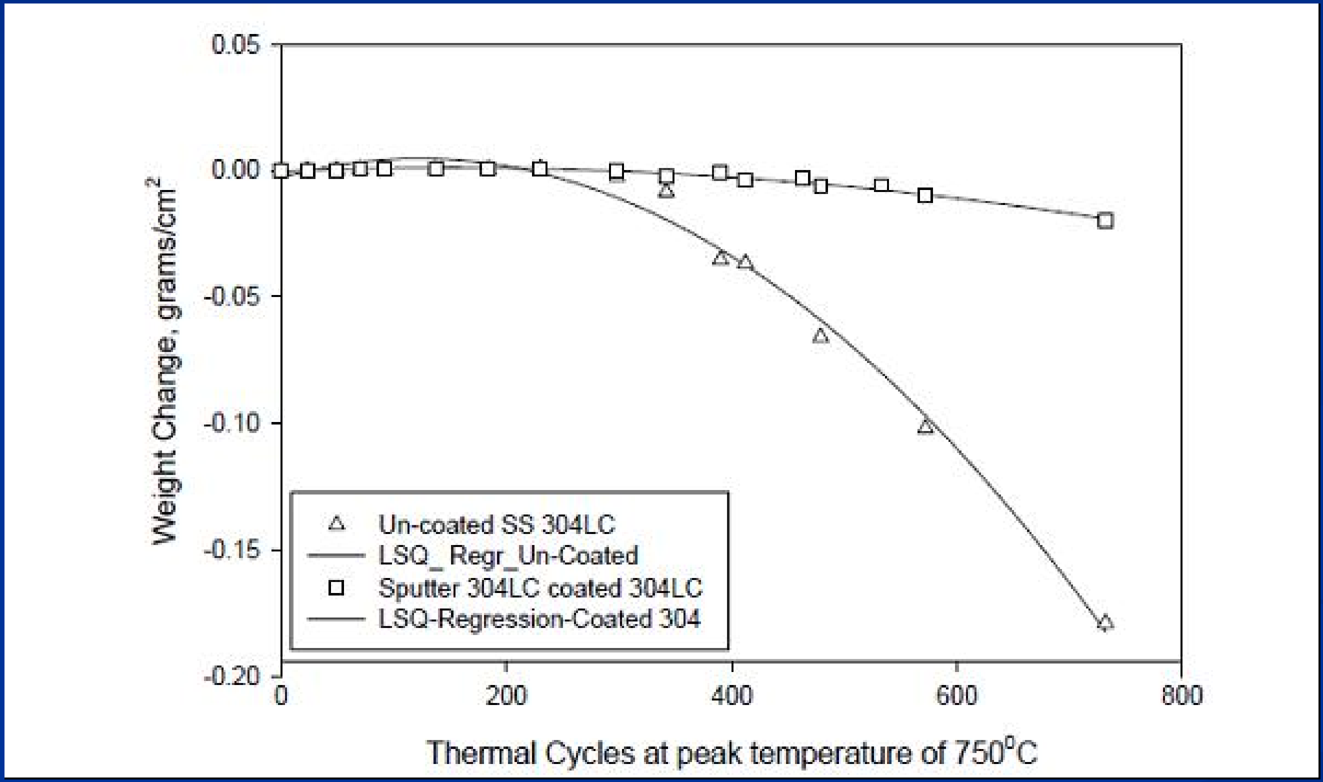
- Coated samples were evaluated for short-term cyclic oxidation behavior up to 700 hours at two peak temperatures of 750 and 1010C.
- Long-term isothermal behavior of coated samples was evaluated at 750C for 1600 hours.
- Coal-ash corrosion resistance of coated and uncoated samples was evaluated at 450C, 650C, and 750C in simulated coal combustion environment.

Microstructural Analysis



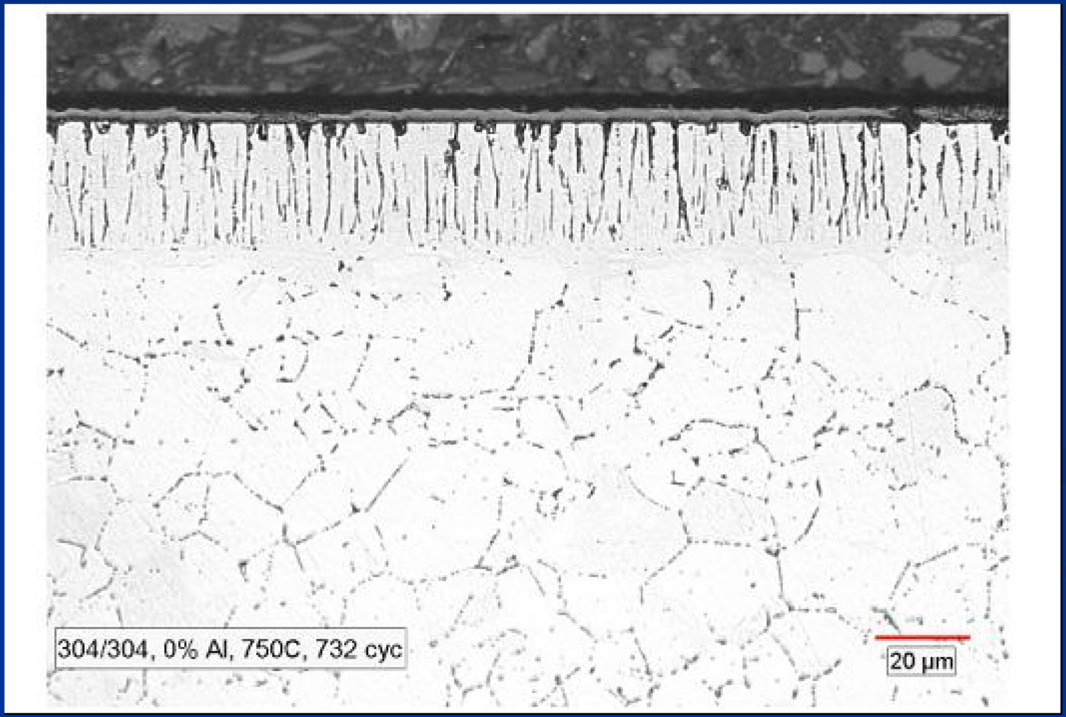
Typical microstructure of as-deposited 304SS on 304SS substrate after electrolytic etching showing columnar grain structure.

Oxidation behavior of nanostructured coatings



- Cyclic oxidation behavior for uncoated and coated samples was almost the same for up to 250 one-hour thermal cycles.
- The weight loss is due to domination of oxide scale spallation during cycling.
- Scale on the sputtered coated specimen is more resistant to spallation.

Microstructural analysis



- Evidence of coating oxidation along columnar grain boundaries.
- No evidence of oxidation at coating/substrate interface.
- Protective oxidation scale can be seen on the outer surfaces of the coating, except in areas where spallation of oxide was noted.

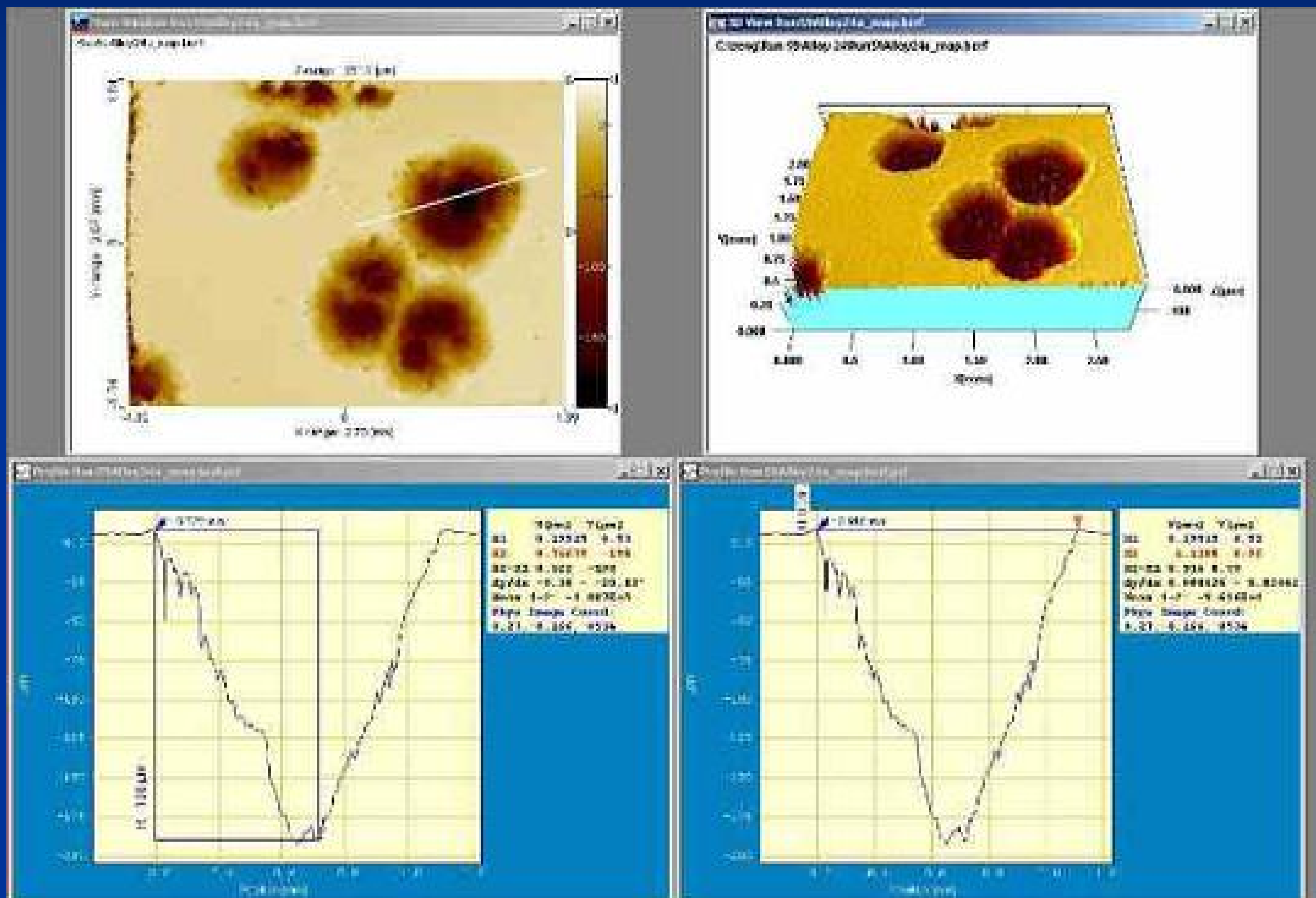
Evaluation of Coal-ash Corrosion Resistance

Test Environment	Ash Composition	Flue Gas Composition	Temperature, °C	Exposure Time, Hours
1	89% oxides + 1% NaCl + 10% Sulfates	1% SO_2 + 99% Air	750	600
2	89% oxides + 10% Sulfates	1% SO_2 + 99% Air	750	1600
3	89% oxides + 1% NaCl + 10%	1% SO_2 + 99% Air	750	1500
4	89% oxides + 1% NaCl + 10% Sulfates	1% SO_2 + 99% Air	450	1600
5		1% SO_2 + 99% Air	650	1500
6		1% SO_2 + 99% Air-NaCl vapor	650	500

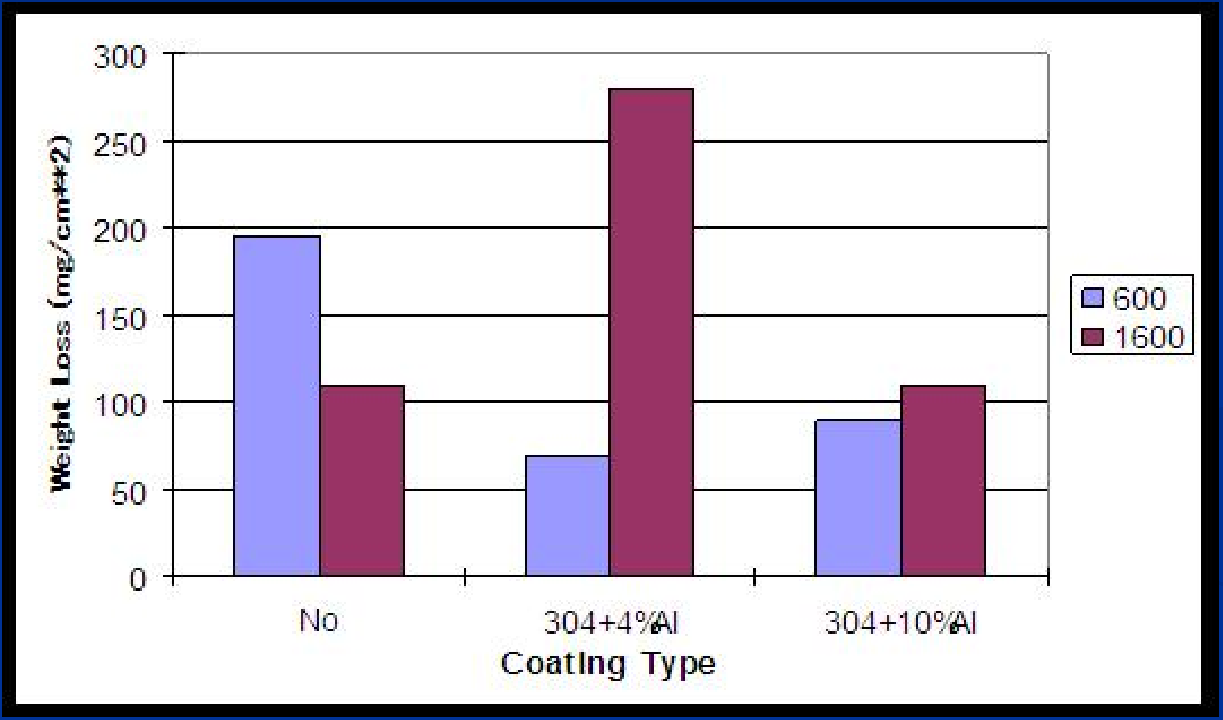
Evaluation of corrosion damage

- Monitoring the weight change
- Measuring the pit depths by a surface profiler from ADE phase shift
- Examining the microstructure with Hitachi S-4700-II Scanning Electron Microscope (SEM)

Typical example of a profile map



Coal-ash corrosion Resistance of Nanostructured coatings – 304 L Steels

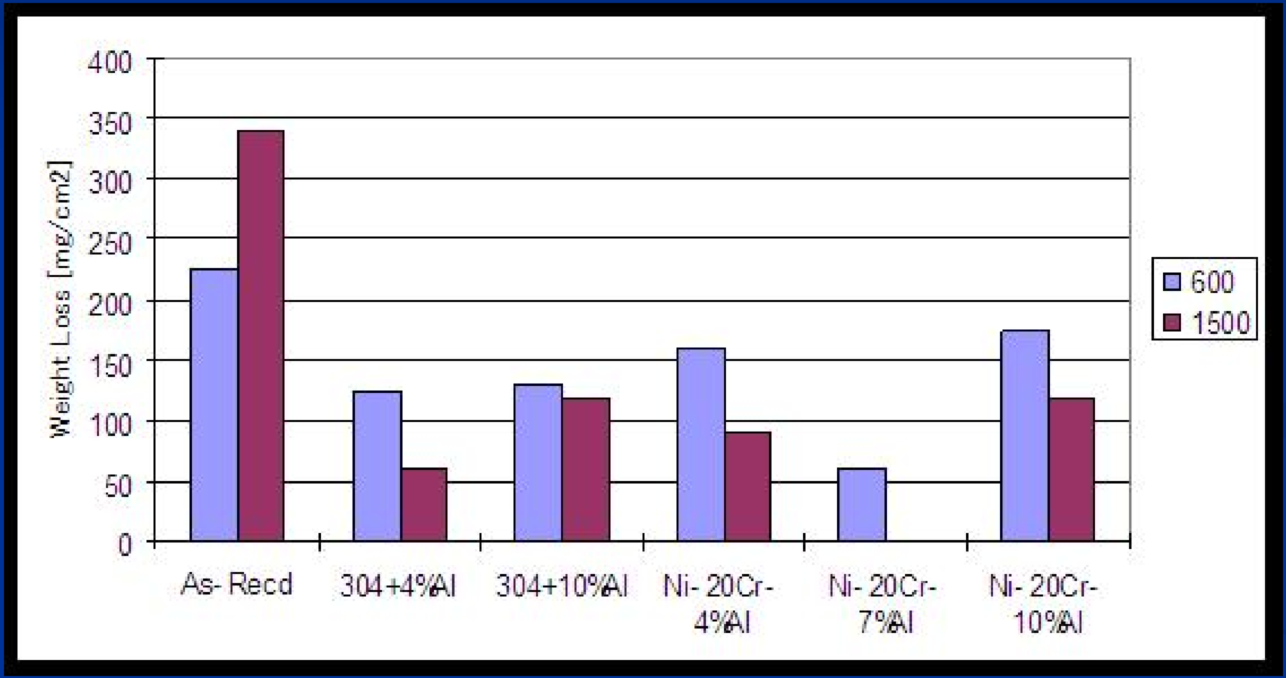


Testing conditions:

- Coal ash: 89% Oxides, 1% NaCl and 10% Sulfates
- 1% SO_2-99%Air
- 750C

Substrate: 304 L Coating: 304+0% Al; 304+4%Al; 304+ 10% Al

Coal-ash corrosion Resistance of Nanostructured coatings – P91 Steels

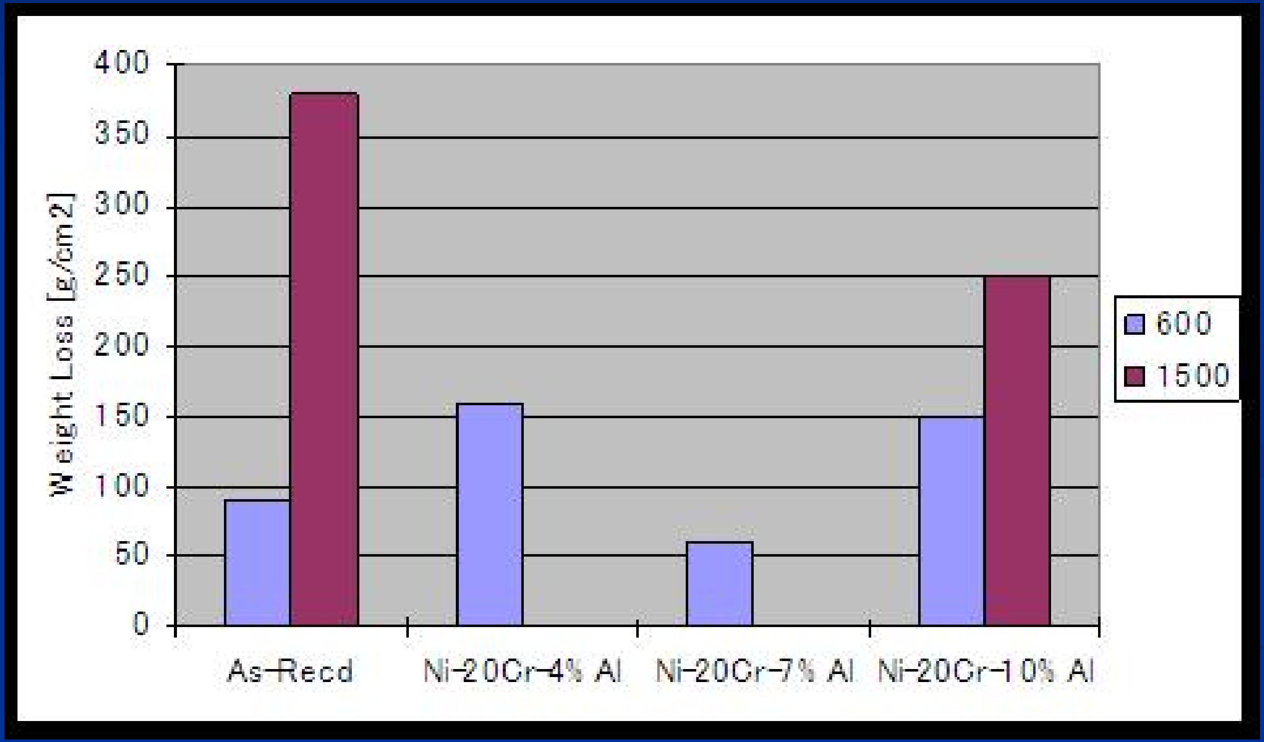


Testing conditions:

- Coal ash: 89% Oxides, 1% NaCl and 10% Sulfates
- 1% SO_2-99%Air
- 750C

Substrate: P91: **Coating: 304+4%Al; 304+10% Al; Ni-20Cr-4%Al; Ni-20Cr-7%Al; Ni-20Cr-10%Al**

Coal-ash corrosion Resistance of Nanostructured coatings – H230

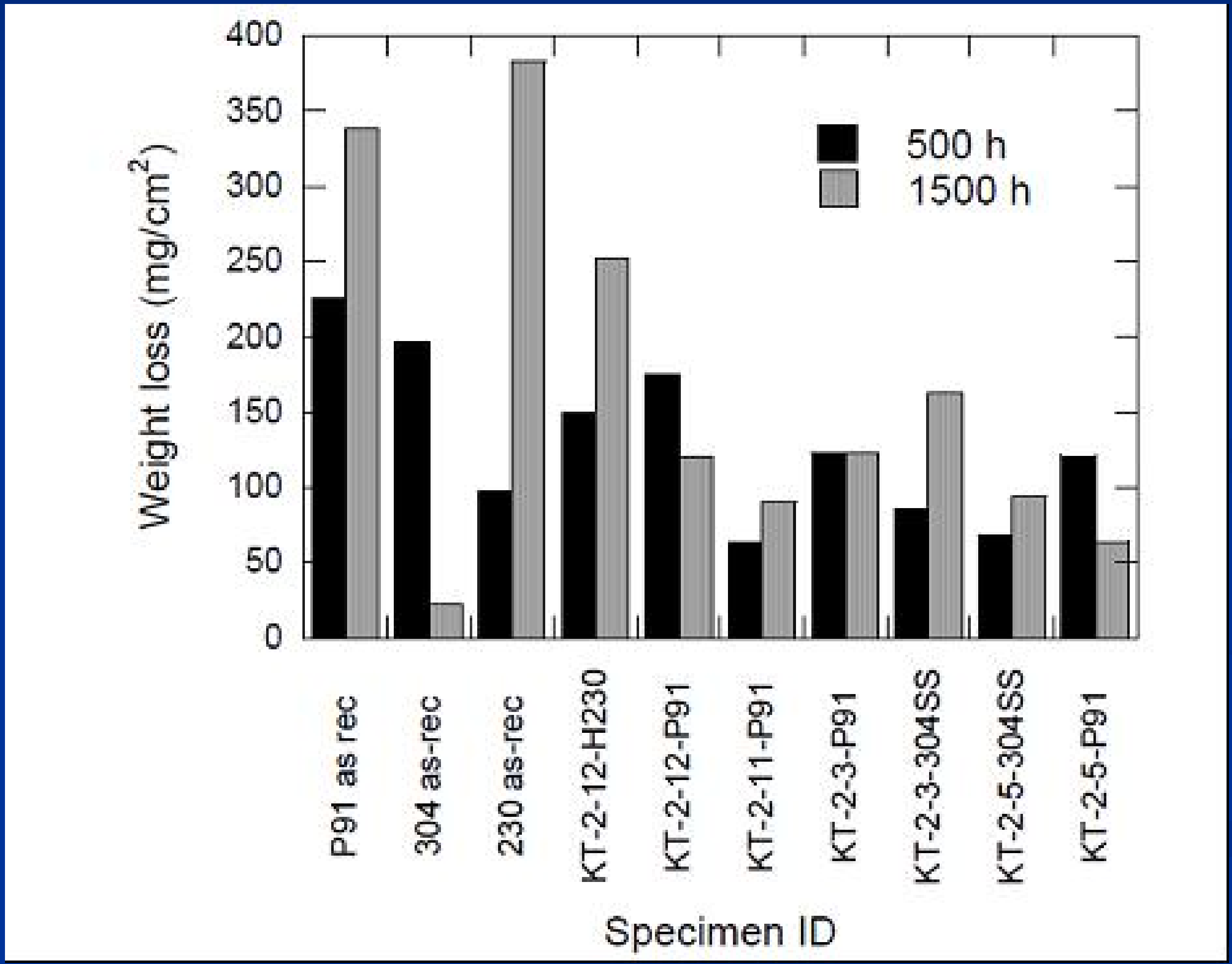


Testing conditions:

- Coal ash: 89% Oxides, 1% NaCl and 10% Sulfates
- 1% SO_2-99%Air
- 750C

Substrate: H230: Coating: Ni-20Cr-4%Al; Ni-20Cr-7%Al; Ni-20Cr-10%Al

Coal-ash corrosion Resistance of Nanostructured coatings

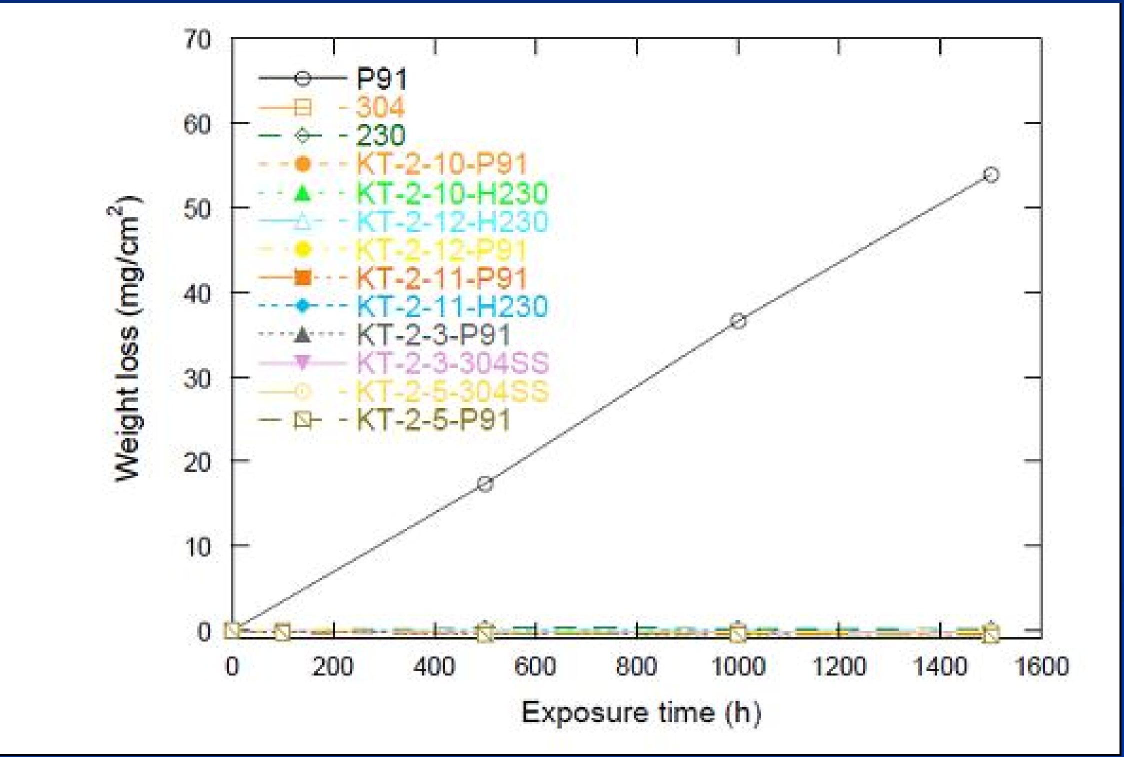


KT-2-12 – 10%Al
KT-2-11 – 7% Al
KT-2-5 – 4% Al
KT-2-3 – 10% Al

Testing conditions:

- Coal ash: 89% Oxides, 1% NaCl and 10% Sulfates + 1% NaCl
- 1% SO_2-99%Air
- 750C

Coal-ash corrosion Resistance of Nanostructured coatings

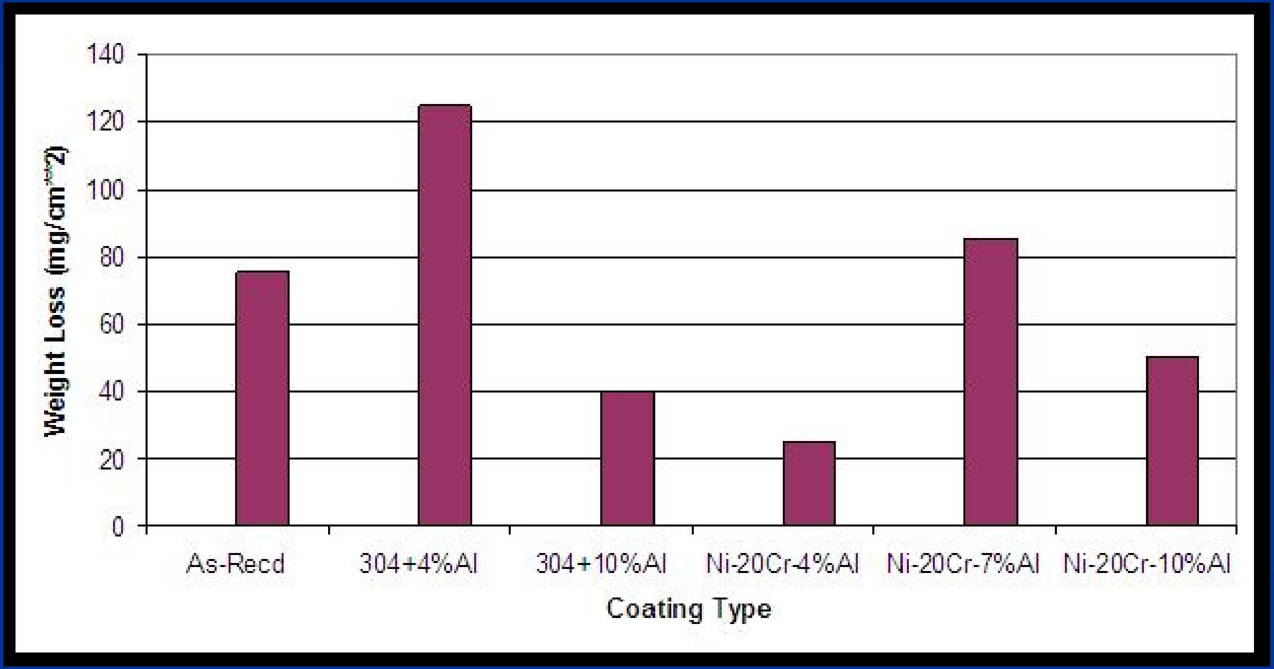


KT-2-12 – 10%Al
KT-2-11 – 7% Al
KT-2-5 – 4% Al
KT-2-3 – 10% Al

Testing conditions:

- Coal ash: 89% Oxides, 1% NaCl and 10% Sulfates + 1% NaCl
- 1% SO_2-99%Air
- 450C

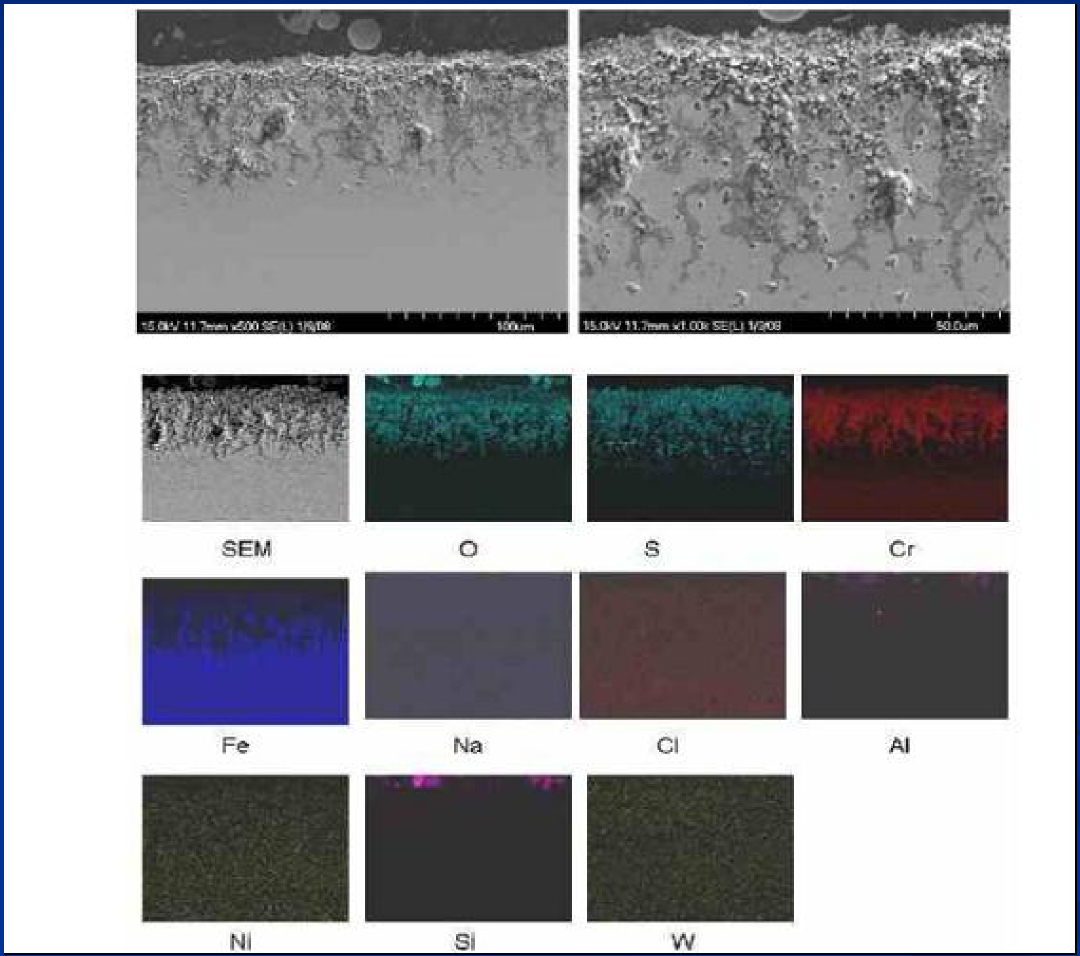
Corrosion Resistance of Nanostructured coatings –P91



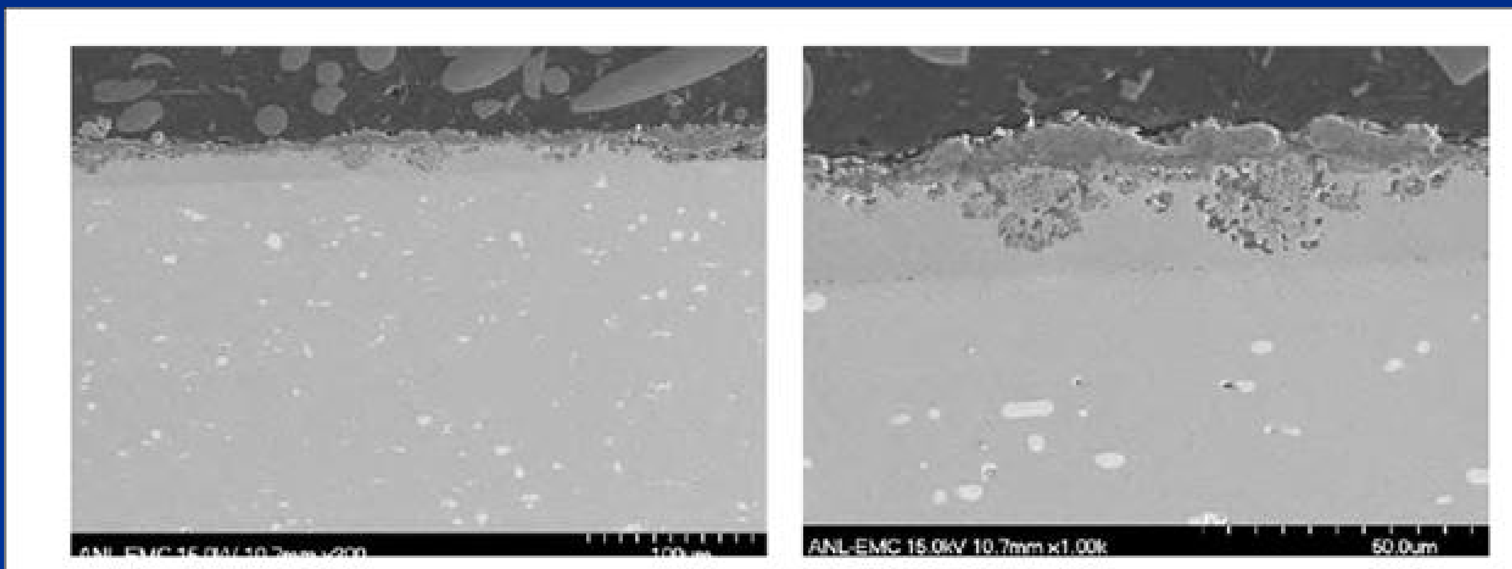
Testing conditions:

- 1% SO_2-99%Air
- NaCl vapor
- 650C
- 500 Hours

Microstructural and EDX analysis of SS304 (10% Al)



Microstructure of H230 with coating of Ni-20Cr-10%Al



Testing conditions: 1% SO_2 and NaCl vapor at 650C after 500 hours of exposure

Conclusions

- Plasma Enhanced Magnetron Sputtering (PEMS) process can be used to deposit nanostructured coatings.
- The coating thickness on the specimens was in the range of 19 to 21 μm. the grain size of the as-deposited Ni-20Cr-4Al, Ni-20Cr-7Al, and Ni-20Cr-10Al coatings were 14.7, 13.2 and 8.7 nm, respectively.
- The Fe-18Cr-8Ni coatings exhibited improved oxide scale spallation resistance compared to the uncoated specimens. A continuous protective Cr-rich, Cr_2O_3 oxide scale was seen on the outer surface of the coating after exposure to thermal cycles, while the un-coated 304L sample exhibited mixed oxides.
- The addition of Al to Fe-18Cr-8Ni coating significantly enhanced oxide scale spallation resistance.

Conclusions

- Evidence of internal oxidation was observed along the columnar grains of the Fe-18Cr-8Ni-4 Al% coating after thermal exposure. A continuous Al-rich oxide scale was seen in the isolated areas on the coating outer surface after thermal cycling.
- The as-deposited Ni-20Cr-xAl exhibited fine columnar grain without any voids between the columns and nano-lamellae with fine transverse cracks.
- Evaluation of P91 and H230 samples tested at 750°C in simulated ash show the formation of an external scale that is predominantly a mixture of sulfide and oxides. It was evident that 10% Al is not sufficient to provide corrosion protection to the sample.

Conclusions

- Evaluation of samples tested in flue gas environment with SO_2 showed an increase in corrosion resistance with increase in aluminum content in the coating.
- Improved corrosion resistance could be obtained with denser coatings. Further optimizations are needed in coating process to deposit denser coatings and to make them viable for long-term use.