COMPUTATIONAL MODELING AND ASSESSMENT OF NANOCOATINGS FOR ULTRASUPERCRITICAL BOILERS

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ABSTRACT

Advanced MCrAl (where M is Fe, Ni, or Co) nanocrystalline coatings (nanocoatings) produced via Plasma Enhanced Magnetron Sputtering (PEMS) technology are being assessed for ultrasupercritical steam boiler applications. In past research, computational modeling was utilized to select the coating composition, but coating defects resulted in poor corrosion performance. Additionally, interdiffusion of aluminum into the substrate compromised coating oxidation performance. In this work, a thin interdiffusion layer was utilized to eliminate aluminum consumption from diffusion with the substrate. Processing studies were also conducted to improve coating quality. The initial oxidation and corrosion test on these optimized coatings show good performance due to minimization of coating defects.

INTRODUCTION

Research on coatings with nanocrystalline grain size (less than 100nm) show these coatings can offer significant performance advantages when compared to traditional coatings of the same composition. Nanocrystalline grain size can enhance diffusion of oxidation/corrosion resistant elements, increased coating adhesion, improved coating toughness, and reduced required coating thickness to achieve corrosion protection[1]. Based on this knowledge, a research project was initiated by the U.S. Department of Energy (U.S. DOE) and the Electric Power Research Institute (EPRI) in 2007 to design and evaluate the use of nanostructured coatings (hereafter referred to as nanocoatings) for fireside corrosion resistant applications in ultrasupercritical (USC) steam boiler waterwalls (ww) and superheaters/reheaters (SH/RH).

BACKGROUND

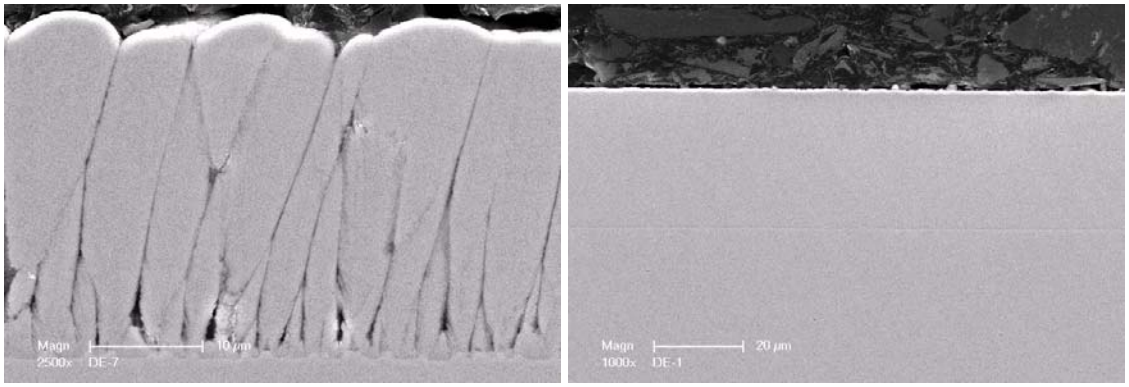
Initial research utilized computational modeling to select coating aim compositions. This included constructing phase diagrams and developing grain growth, sintering, and diffusion models. The modeling pointed to the MCrAl (where M is Fe, Ni, or Co) alloy system as a starting point with a coating composition having a minimum of 4-5wt% aluminum (Al). To ensure a sufficient Al reservoir, the optimal coating composition from the modeling work was found to be Fe-30/40Ni-25Cr-10Al[2].

The process utilized for coating was plasma enhanced magnetron sputtering (PEMS) which is a physical vapor deposition (PVD) process. The advantages of PEMS is that it utilizes ion sputter cleaning to fully remove surface contaminants to produced good coating adhesion, the plasma generated during the process fills the entire chamber greatly increasing current density to the substrate, and the resultant coating microstructure can be tailored to achieve grain sizes less than 100nm (i.e. produces nanocoatings). The targets utilized in the process were obtained from commercial materials to produce four candidate coatings close to the composition of the model inputs. This included 2 iron-based coatings, one nickel-based coating, and one cobalt based coatings as follows:

- 310+Al (Fe-25Cr-20Ni-10Al)
- Haynes 120+Al (Fe-37Ni-25Cr-10Al)
- Haynes 160+Al (Ni-29Cr-3Si-10Al)
- Haynes 188+Al (Co-22Ni-22Cr-14W-10Al)

INITIAL RESULTS

Initial processing studies were conducted utilizing the PEMS process and detailed characterization and cyclic oxidation testing was performed[3]. Figure 1 compares a scanning electron microscope (SEM) image of a less-than-desirable coating structure (a) to a preferred coating structure (b). Large microscopic features are observed in (a) while (b) shows a featureless structure (finer than resolution of SEM). The optimum processing conditions were obtained for the coatings utilizing process iterations combined with adhesion tests and destructive microstructural evaluation. X-ray diffraction was used to confirm the grain size of the coatings was less than 100nm. Cyclic oxidation testing was also performed on the coatings. Figure 2 shows the microstructure of the coating and substrate after approximately 1000 hours at 750°C (990cycles). The formation of FeAl precipitates in the substrate is observed. Chemical composition of the coating showed loss of Al in the coating. Based on these initial coating trial results, Al consumption with the substrate was identified as a major barrier to achieving acceptable coating lifetime at higher temperatures.



(a) *(b)*

Figure 1. (a) non-optimum coating condition (b) optimum coating condition showing dense adherent coating

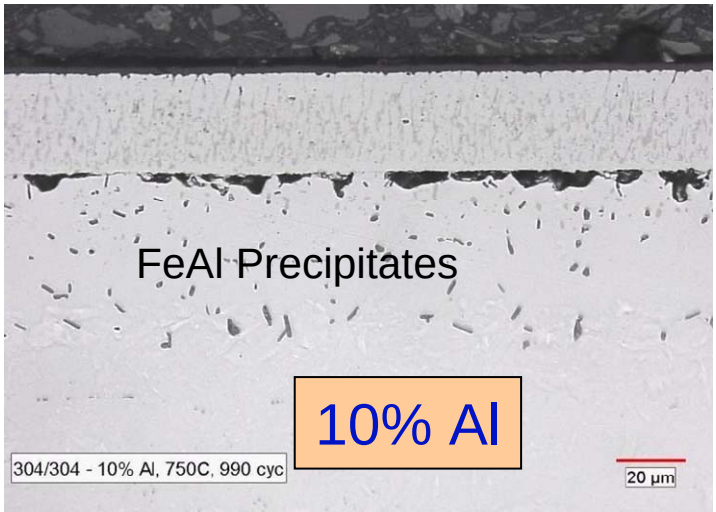


Figure 2. Microstructure of Fe-based nanocoating after cyclic oxidation testing at 750°C for 990cycles (~1000 hrs) showing the formation of internal FeAl precipitates due to interdiffusion of Al with substrate

A series of samples were also produced for laboratory fireside corrosion testing[4]. The testing conditions were chosen based on previous experience in testing materials and coatings for USC ww and SH/RH conditions. 1000 hour tests were performed in a simulated eastern bituminous coal condition. In addition to the nanocoatings produced as part of this program, commercial 'nanocoatings' were also evaluated. Extensive results and discussion on this work can be found in reference 4. Figure 3 shows selected specimens from the post-test metallographic evaluation after ww testing and figure 4 shows post-test results at SH/RH conditions. Figures 3 and 4 provide a good general picture of the finding which showed for:

- Waterwall (ww) conditions
    - Commercial nanocoatings provided little-to-no protection with significant penetration of oxide and sulfide species

    - DOE Nanocoatings showed ‘bulk’ corrosion resistance but coating defects allowed for oxide and sulfide species to penetrate the coating (in some cases to the substrate)
- Superheater/Reheater (SH/RH) conditions
    - Commercial nanocoatings displayed poor corrosion resistance being completely consumed during testing
    - All DOE nanocoatings were severely corroded with localized wastage in the substrate material
    - Some DOE nanocoatings also displayed, similar to oxidation test, interdiffusion between the coating and substrate

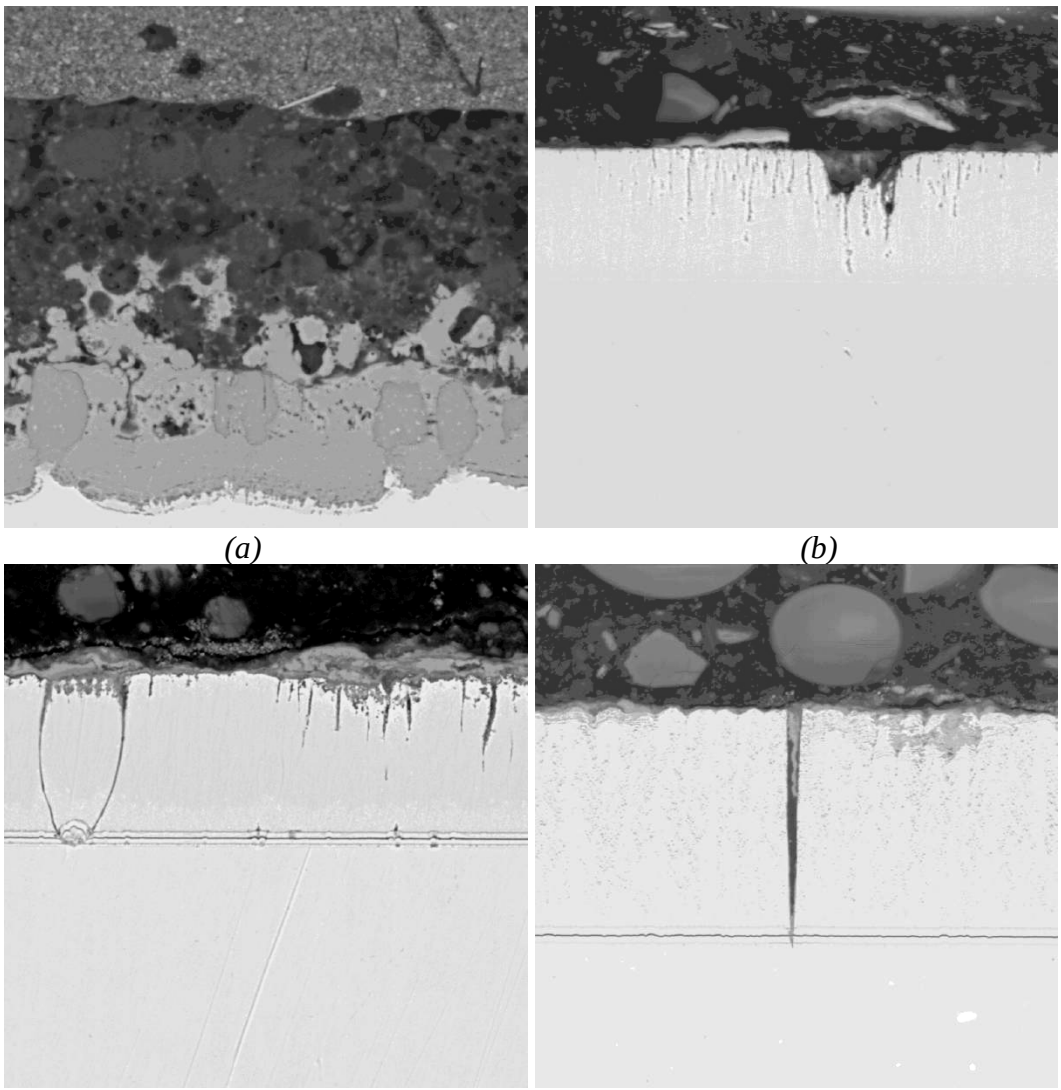


Figure 3. Waterwall fireside corrosion test results after 1000 hrs at 524°C (975°F) showing commercial coating (a) did not provide any corrosion behavior and nanocoatings from this research (b), (c), and (d) show ‘bulk’ protective behavior but corrosion penetration to the substrate has occurred at coating defects including columnar ‘cauliflower’ defects (c) and cracks (d)

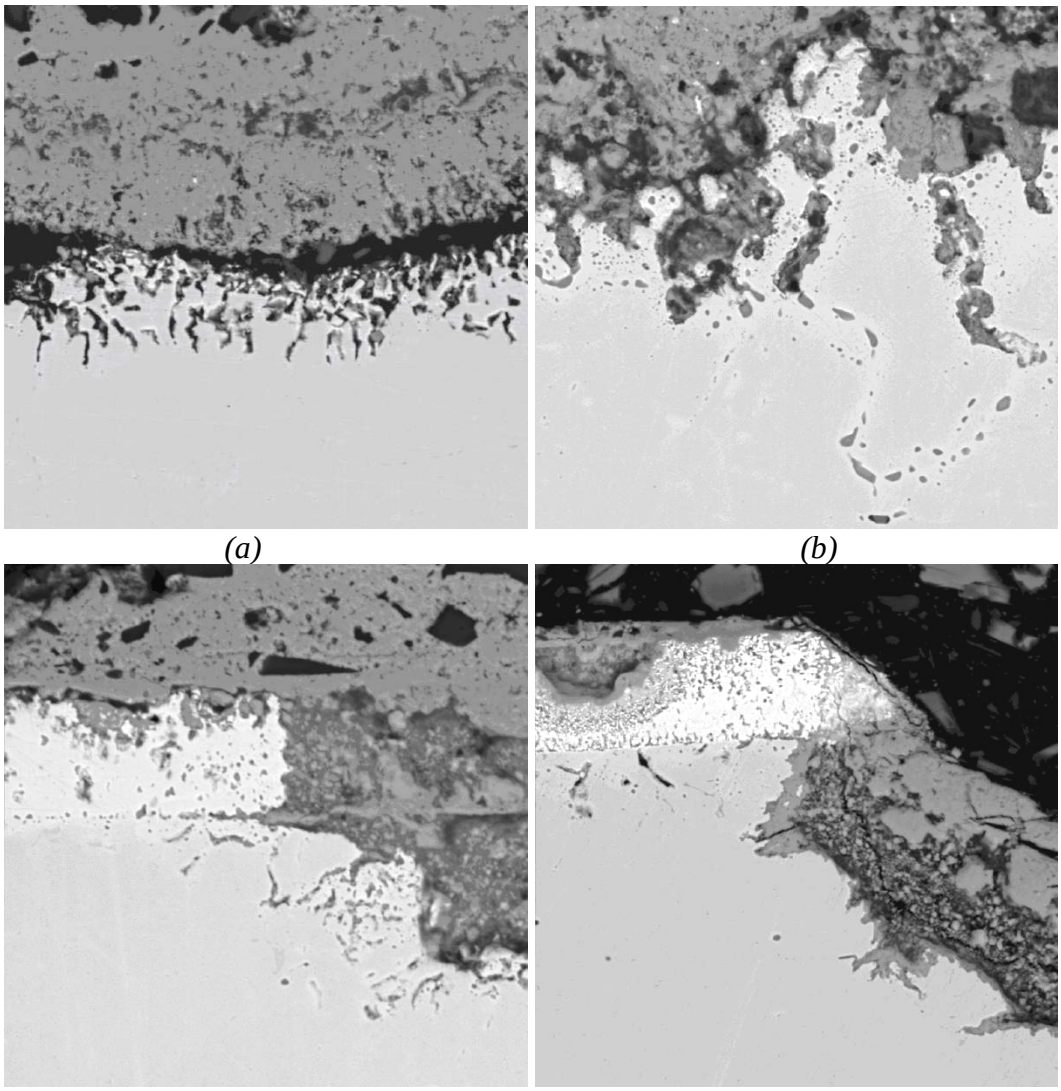


Figure 4. SH/RH fireside corrosion test results after1000 hrs at 700°C (1300°F) showing commercial coating (a) was completely consumed and nanocoatings from this research (b), (c), and (d) did not show widely protective behavior due to coating defects

Based on these fireside corrosion test results, it was clear that poor coating quality 'short-circuited' the potential for good fireside corrosion protection. Coating defects included columnar grain boundaries (cauliflower-type defects) and cracks

CURRENT RESEARCH

Two major issues needed to be addressed based on the initial research: interdiffusion of Al into the substrate and coating quality and reproducibility. Interdiffusion of Al into the substrate was observed at temperatures expected for USC SH/RH conditions thus limiting the potential life of the coating. Although optimum process parameters were used for

producing the coatings, cracking and cauliflower-type defects were observed in all the nanocoatings short-circuiting potential good corrosion behavior.

To address interdiffusion of Al, research was conducted to utilize a thin interlayer to act as a diffusion barrier with the substrate. Variations of AlN, TiN, and TiSiCN were evaluated with accelerated cyclic oxidation testing a 1010°C and at 750°C. The results showed that a thin (less than 1mm) layer of TiN was effective at shutting-off interdiffusion of Al. 2,000 hour tests at 1010°C showed the nanocoatings with the TiN layer had very little Al consumption (similar to typical alumina forming coatings) whereas the coating without the TiN had nearly complete Al consumption after 500 hours. Figure 5 shows the microstructure of the coating and substrate after cyclic oxidation testing at 750°C. The difference is clear when compared to figure 2, no FeAl precipitates were seen after exposure. Consistent with this. at 750°C, the presence of the TiN inter layer has completely shut-off interdiffusion which was confirmed with chemical composition measurements showing no change in Al content pre and post-test.

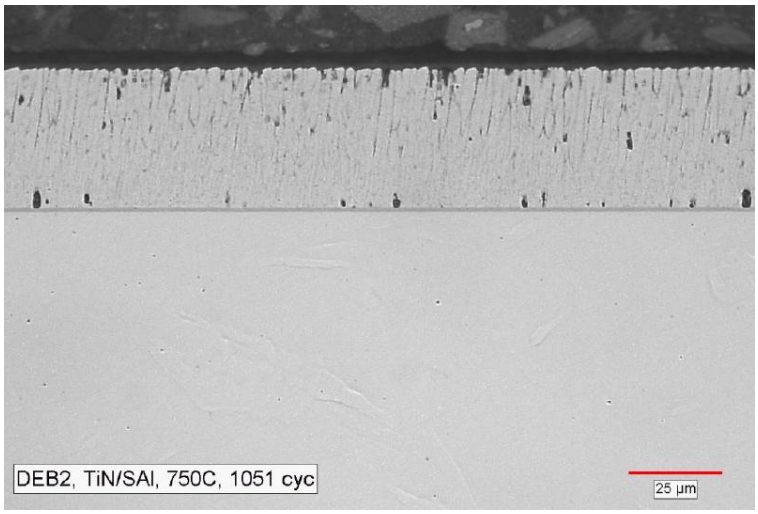


Figure 5. Microstructure of Fe-based nanocoating with TiN interlayer after cyclic oxidation testing at 750C. No FeAl precipitates are observed (compare to figure 2). Interdiffusion of Al is stopped.

To address coating quality and reproducibility, a series of processing studies were conducted. This work showed that careful control of processing parameters, coating cracking could be eliminated but cauliflower defects still persisted. High power impulse magnetron sputtering was then evaluated as an alternate processing technique. The process did produce crack-free coatings, but coating adhesion was very poor and the process was abandoned. The final evaluation was to use a pulsed-DC power supply with the PEMS process. This gave the best results. Further modification to the process utilized intermittent Ar-sputter cleaning and resulted in coating which were free from cracks, had minimal cauliflower defects, and eliminated through-thickness defects. To further ensure reproducibility, 10 coating trials were conducted. The assessment of these trials found:

- Consistent chemical composition of the coatings
- Consistent grain size of the coatings (4 to 8 nm)
- No cracking in any coatings
- The maximum defect area fraction was 1.2%

Based on these results, the process is considered repeatable.

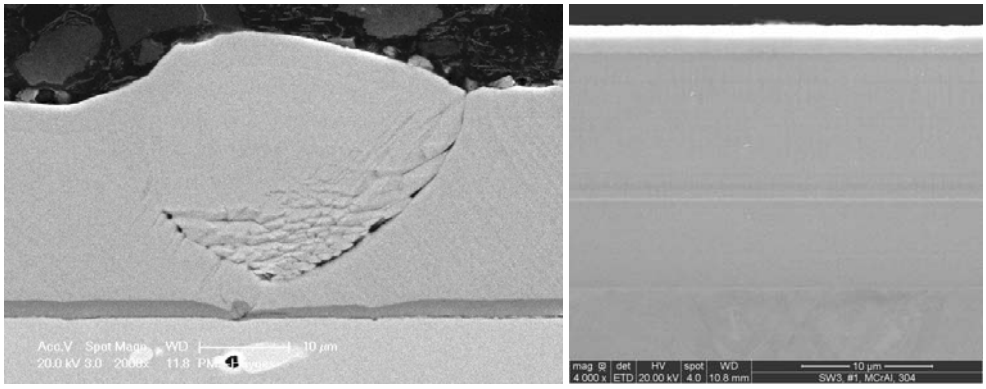
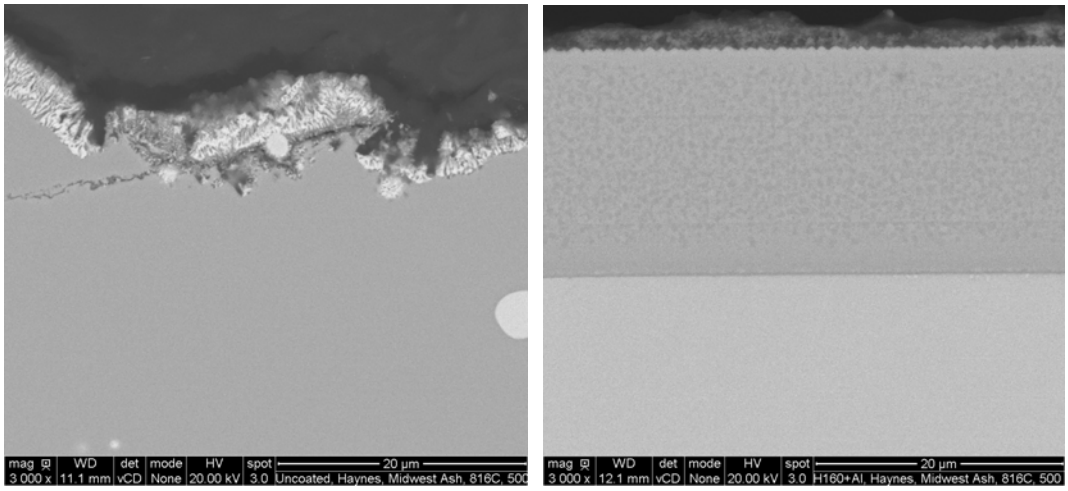


Figure 6. Cross-sectional SEM images of nanocoating utilizing the PEMS process with a pulsed DC power supply and intermittent Ar-sputter cleaning, note the defect is not through-thickness

Based on the 'new' optimized process, samples were produced and are currently being subjected to laboratory fireside corrosion testing. Test conditions were chosen to match the earlier test program for comparison with original samples and work on USC alloys and weld overlay from prior research. Testing is planned for 1,000 hours at SH/RH conditions. After 500 hours, two samples were removed. Figure 7 shows cross-sectional images for an uncoated nickel-based alloy substrate and one nanocoating. No corrosion is observed on the nanocoating while the uncoated sample shows significant hot corrosion wastage.



(a) *(b)*

Figure 7. (a) uncoated and (b) optimized nanocoating after 500 hours exposure in laboratory corrosion tests at SH/RH conditions. Uncoated sample shows corrosion while nanocoating is still intact with no observable wastage.

CONCLUSIONS

Nanocoatings based on the MCrAl system designed by computational methods and produced with the PEMS process are being assessed for fireside corrosion resistance in waterwall and superheater/reheater conditions in USC boilers. Two major findings from the initial research were found to limit the usefulness of the coatings. These were: Al consumption in the substrate material which reduced Al in the coating thus reducing coating lifetime, and coating defects which served as preferential sites for corrosion initiation. To address the issue of internal Al consumption, a thin TiN interdiffusion barrier layer was developed, and cyclic oxidation tests show it shuts-off diffusion of Al to the substrate. For coating quality, it was necessary to optimize the coating parameters, utilize a pulsed DC power supply, and intermittently Ar-sputter clean to achieve crack-free coating without through thickness defects. The current corrosion test results on these optimized coatings are showing good performance.

ACKNOWLEDGEMENTS

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REFERENCES

[1] *State-of-Knowledge Review of Nanostructured Coatings for Boiler Tube Applications*, EPRI Palo Alto, CA: 1014805.

[2] *Computational Modeling and Assessment of Nanocoatings for Ultra Supercritical Boilers: Technical Report, Reporting Period: August 2007 thru June 2008.* Report Number: FC26-07NT43096-01 OSTI ID: 933025

[3] *Computational Modeling and Assessment of Nanocoatings for Ultra Supercritical Boilers: Task 3 Technical Report Processing of Advanced MCrAl Nanocoating Systems.* Report Number: FC26-07NT43096-02 OSTI ID: 962674

[4] *Computational Modeling and Assessment of Nanocoatings for Ultra Supercritical Boilers- Task 4 Technical Report: Fireside Corrosion Testing.* Report Number: FC26-07NT43096-03 OSTI ID: 974655