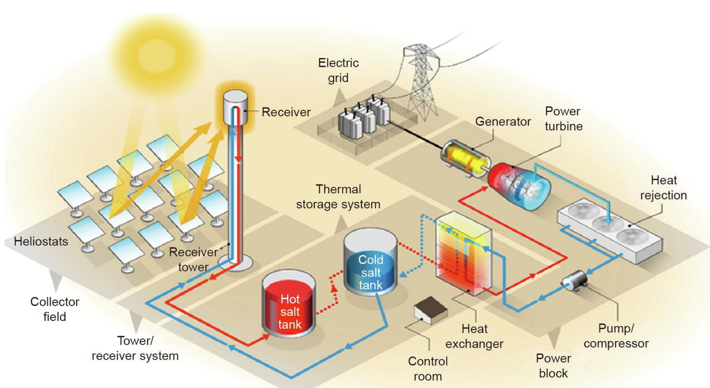
Corrosion Behaviors of Diamond Coated Stainless Steel 316 in Molten Nitrate Salts

Xin Chen[1], Zhipeng Wu[2], Bai Cui[1], Yongfeng Lu[2]

[1]Department of Mechanical & Materials Engineering, [2]Department of Electrical Engineering

Research Background

- Thermal energy storage is a key performance parameter for improving the viability of the concentrated solar power (CSP) plants.
- Molten nitrate salts (MS) have been extensively used in CSP to transfer and store heat given their unique thermal properties.
- The construction of the hot tank requires the use of materials with good corrosion resistance.



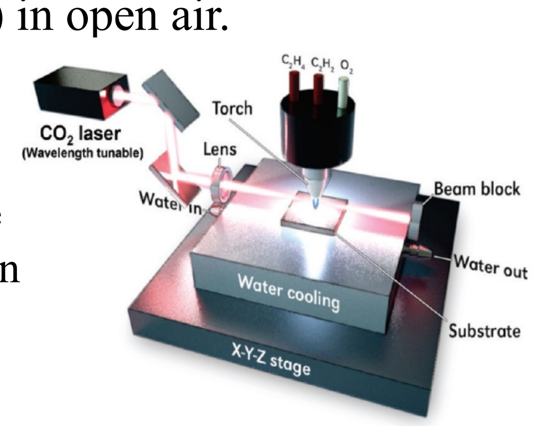
A state-of-the-art power tower second generation CSP plant with molten nitrate salts as TES/HTF materials

Motivation and Objectives

- Fast deposition of large-area diamond coatings on curved surfaces of pipes and vessels in open air using LCVD with interface engineering to improve the adhesion of diamond coatings on metallic substrates.
- Characterizing the microstructures of diamond coatings and diamond/substrate interfaces
- Determining the molten-salt corrosion resistance, wear resistance, and thermal conductivity of the diamond coatings.

Experimental Setup

- Diamond films were deposited stainless steel (SS) 316 using a laser-assisted combustion chemical vapor deposition (CVD) in open air.

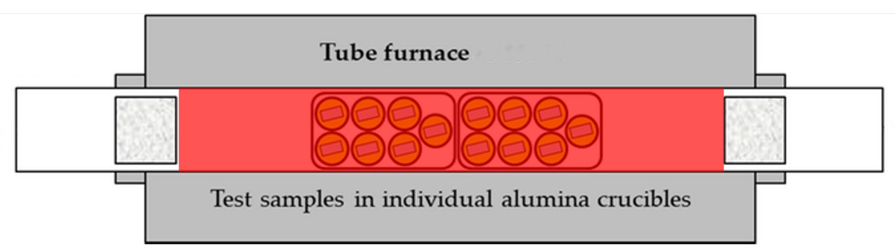


Schematic setup for the laser-assisted combustion CVD of diamond films

Compositions of SS 316

Element	C	Cr	Mn	Fe	Mo	Ni	P	S	Si
Percentage	0.08	18	2	82	3	14	0.045	0.03	1

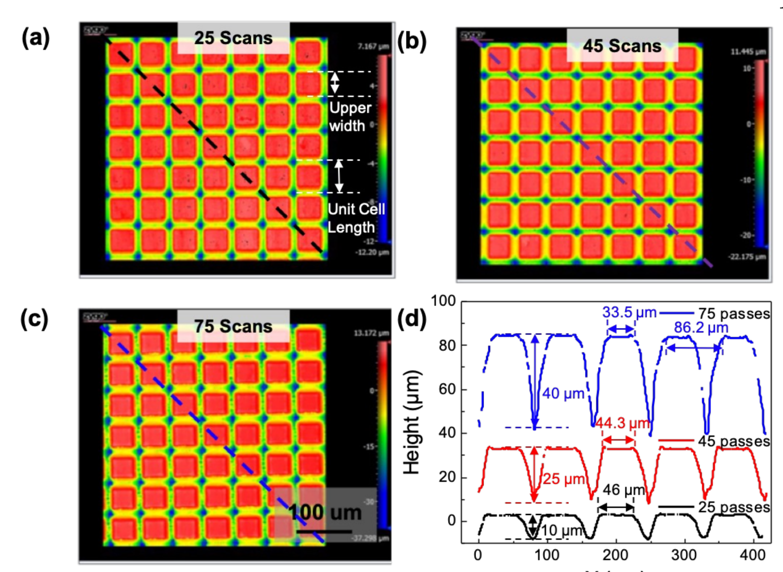
- The corrosion test was performed in a horizontal tube furnace with samples placed in alumina boats and covered with the salt mixture. The boats were placed in the hot zone of the furnace.



Schematic setup for the corrosion test in the molten binary nitrate salt

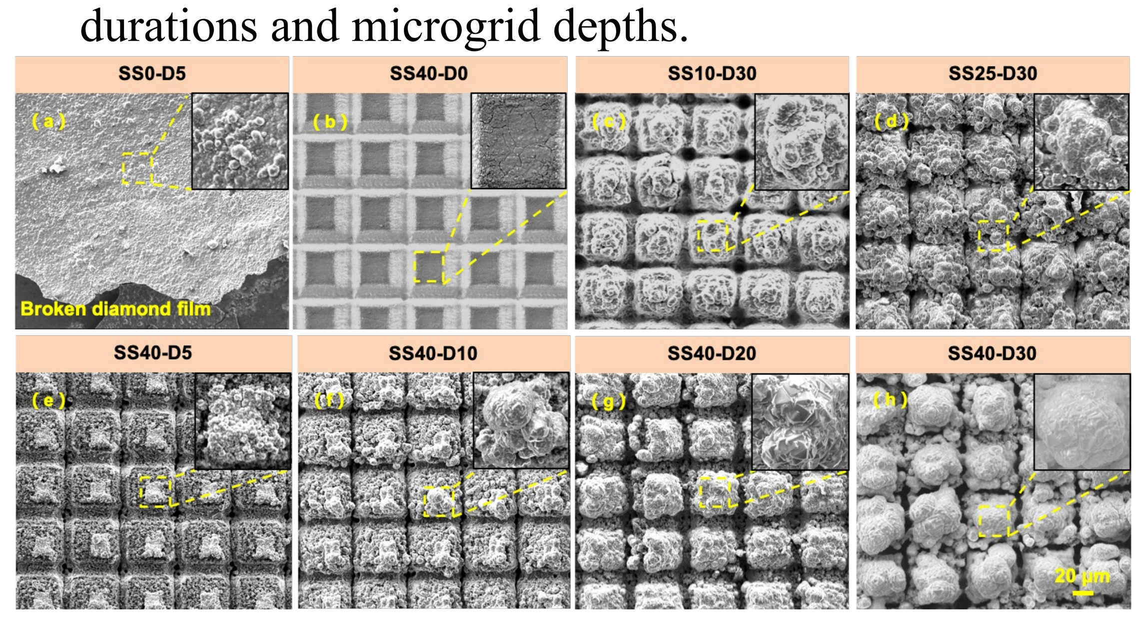
Characterization of Diamond Films

- Morphologies observations of the fs laser textured SS 316 substrate surfaces with different scan passes.



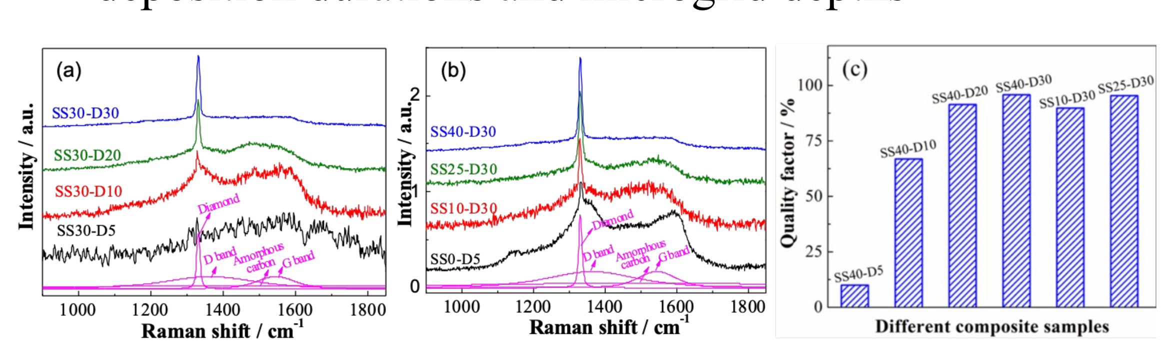
Zygo profiles of fs-laser textured SS 316 substrates with 25, 45 and 75 scan passes

- Microstructures of the diamond coatings deposited on the SS 316 substrates with different deposition durations and microgrid depths.



SEM micrographs of the diamond coatings deposited on the fs-laser textured SS 316 substrates.

- Raman characterization of the diamond coatings deposited on the SS 316 substrates with different deposition durations and microgrid depths



Raman spectra and calculated diamond quality factor

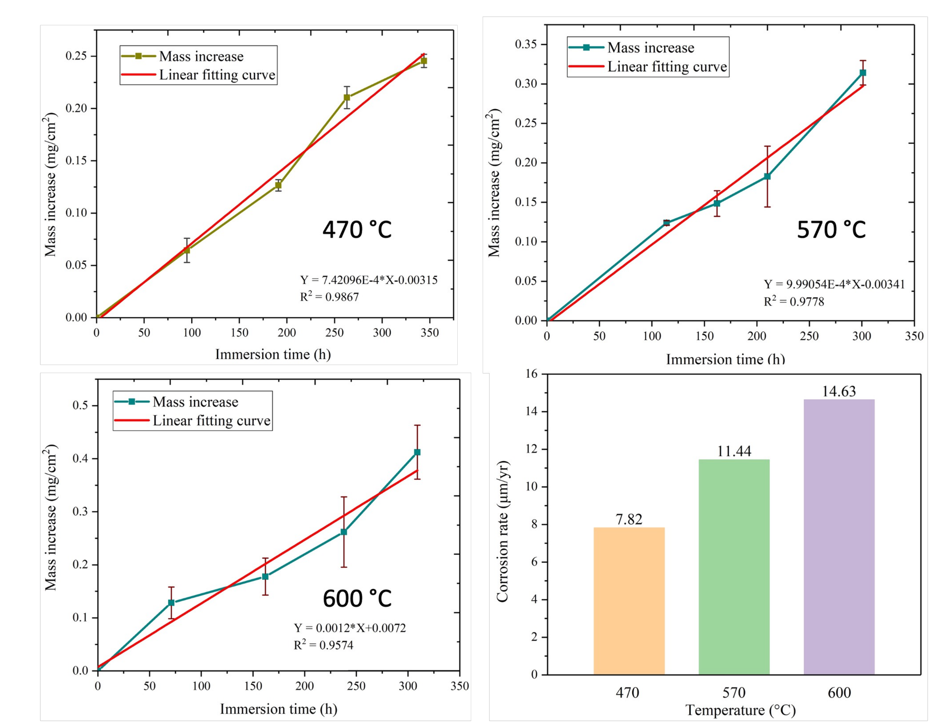
Corrosion Behaviors

- Corrosion rate (CR):

$$CR(\mu m/yr) = \frac{87600\Delta m}{\rho t}$$

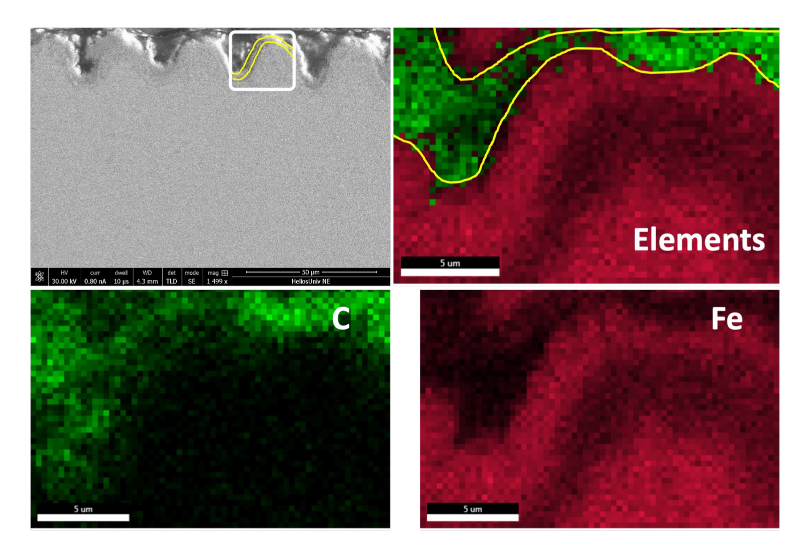
Δm – descaled mass loss per unit area (mg/cm²);
ρ – density (g/cm³): $\rho = 7.99$g/cm³; t – corrosion time (h).

- In the binary nitrate mixtures, the annualized rates were found to be between 6 and 15 $\mu m/yr$ for the bare 316 specimens at 470, 570 and 600 °C.



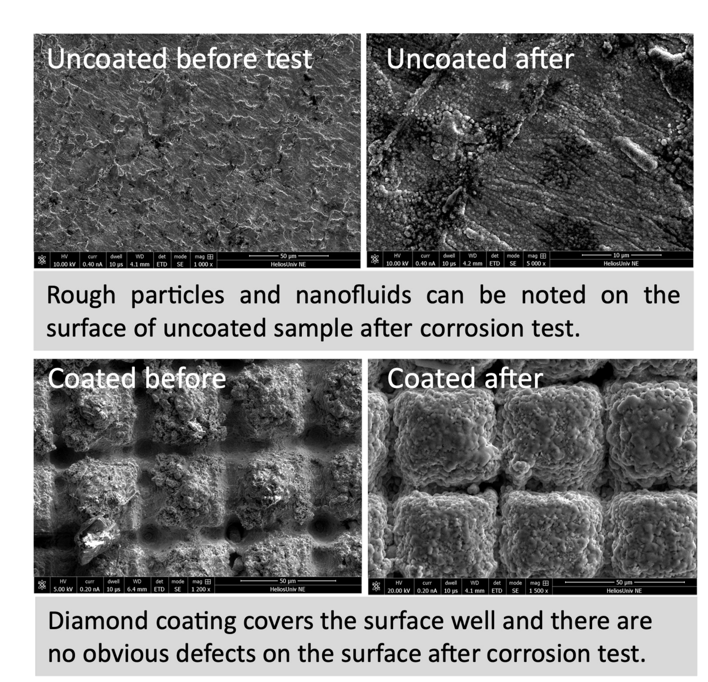
Corrosion test of bare 316 samples at different temperatures

- The SEM micrograph and EDS mapping show interface between substrate and diamond film, indicating a good adhesion.

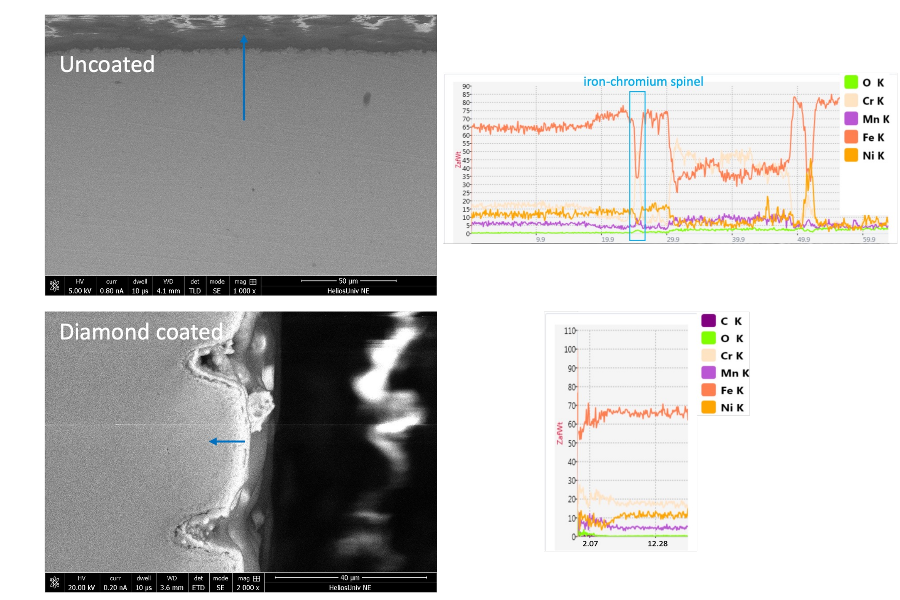


Cross-section microstructure of interface and EDS mapping

- The diamond coated (fs 30 scans 10 min) and bare 316 SS samples were exposed to 500°C for 15h in molten nitrate salt.



- EDS line scan for uncoated sample shows that the oxide was comprised of an iron oxide layer over a layer of iron-chromium spinel. But there are no generation of iron oxide layer on diamond coated sample.
- These results prove the protective behavior of diamond coatings.



EDS line scan of uncoated and diamond coated sample

Corrosion Mechanism

Oxidation process includes peroxides O_2^{2-}, and superoxides, O_2^-, which are formed by reactions between the nitrate and nitrite constituents (at higher temperature nitrite can disassociate to form oxide anions O^{2-}) of the molten salt.

$$O^{2-} + NO_3^- \rightleftharpoons NO_2^- + O_2^{2-}$$

$$O_2^{2-} + 2NO_3^- \rightleftharpoons 2NO_2^- + 2O^{2-}$$

The corrosive effect of these salts is based on the following reduction reaction:

$$NO_3^- + 2e^- \rightleftharpoons NO_2^- + O^{2-}$$

Which results in the oxidation of iron atoms that diffuse from the material:

$$Fe + O^{2-} \rightleftharpoons FeO + NO_2^- + 2e^-$$

$$3FeO + O^{2-} \rightleftharpoons Fe_3O_4 + 2e^-$$

$$2Fe/Cr + 3O^{2-} \rightleftharpoons (Fe,Cr)_2O_3$$

Acknowledgement

This project was supported by the Nebraska Public Power District through the Nebraska Center for Energy Sciences Research at the University of Nebraska-Lincoln.

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