MATERIALS ENGINEERING

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"The Stability of, and Corrosion by, Earth-abundant Molten Chlorides for Use in High-temperature Thermal Energy Storage"

By

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Purdue MSE Ph.D. Final Exam

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ABSTRACT

Concentrated solar power (CSP) is a technology that utilizes focused sunlight to heat a high-temperature medium (such as a molten salt). Heat from this medium can be transferred to a working fluid (such as supercritical CO_2) that is then used to drive a turbine to generate electricity. Alternatively, the hot medium/fluid can be pumped into tanks for thermal energy storage (TES), for heat extraction later to generate dispatchable electricity and/or for electricity production at night or on cloudy days. By increasing the fluid temperature to $\geq$750°C and utilizing TES, CSP can become more cost competitive with fossil-based electricity production. Current CSP systems utilize molten nitrate salts for heat transfer and TES that are known to thermally degrade at temperatures >600°C. To achieve temperatures $\geq$750°C, molten chloride salts, such as ternary $MgCl_2$-KCl-NaCl compositions, are being considered as heat transfer and thermal energy fluids for next generation CSP plants due to their higher temperature stability, low cost, and availability.

In this work, it was demonstrated that $MgCl_2$-containing molten salts are prone to oxidation in ambient air at 750°C, which can enhance corrosion of the containment materials and alter the thermophysical properties of the fluid. An alternative, low-cost, earth-abundant, $MgCl_2$-free, oxidation-resistant molten salt, a eutectic $CaCl_2$-NaCl composition, was developed, along with a corrosion mitigation strategy, to enable the slow growth of protective oxide layers on metals that are resistant to dissolution by such $MgCl_2$-free molten chloride salts.

This strategy was expanded to other low-cost, oxidation resistant compositions, such as eutectic $BaCl_2$-$CaCl_2$-KCl-NaCl with tailored chemical and thermophysical properties for CSP and TES. The melting temperature, heat capacity, oxidation resistance, and crystallization behavior were measured for eutectic a $BaCl_2$-$CaCl_2$-KCl-NaCl(17.5-47.8-3.3-31.4 mol%) (BCKN) salt and a $MgCl_2$-KCl-NaCl (40-40-20 mol%) salt. BCKN salt was shown to have a similar melting temperature while having a higher heat capacity and far better oxidation resistance.

The corrosion of the nickel-based superalloy Haynes 214 was studied in molten $MgCl_2$-KCl-NaCl (40-40-20 mol%) salt at 750°C under inert atmosphere conditions using a custom-built rotating-disc corrosion testing apparatus that maintained laminar fluid flow on the sample. Non-protective external Cr-, Al-, and Mg- oxide layers were formed on Haynes 214 that were prone to spallation. Internal oxidation of Al was also observed along with Cr depletion zones within Haynes 214. Corrosion kinetics were evaluated to quantify the role of fluid flow for application of this alloy for use in containment and transportation of this molten chloride salt.

Date: Tuesday, April 11, 2023
Time: 2:30 P.M.
Place: ARMS 1109 or via Webex:
https://purdue.webex.com/meet/sandhage?_ga=2.208743122.1745866781.1678929685-1932784001.1582931178

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