

Rehydration of Molten Chloride Salts and Its Impact on SS316H Corrosion for Molten Salt Reactor Applications

Seol Kim^{a,b}, Hyeonwoo Kim^c, Joonha Park^{a,b}, Seokmin Yoon^{a,b}, Dokyu Kang^a, Taeho Kim^{a,b}, Chang Hwa Lee^{a,b}, Sangtae Kim^c, Eun-Young Choi^{a,b*}

^aKorea Atomic Energy Research Institute, 111, Daedeok-daero 989beon-gil, Yuseong-gu, Daejeon 34057, Republic of Korea

^bDepartment of Nuclear Science and Technology, University of Science and Technology, 217 Gajeong-ro, Yuseong-gu, Daejeon 34113, Republic of Korea

^cDepartment of Nuclear Engineering, Hanyang University, 222 Wangsimni-ro, Seongdong-gu, Seoul 04765, Republic of Korea

*Corresponding author: eychoi@kaeri.re.kr

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1. Introduction

Molten chloride salts are promising heat transfer and storage media for high-temperature energy systems, including next-generation nuclear reactors and concentrated solar power plants, owing to their high thermal stability and low cost [1]. A major barrier to their industrial deployment, however, is corrosion of structural alloys, which is strongly aggravated by trace moisture impurities in the salt [2]. Consequently, prior research has predominantly focused on thermal dehydration treatments to remove moisture prior to high-temperature operation [3], based on the presumption that higher temperature invariably drives further moisture loss. This presumption, however, has rarely been examined across the solid-to-liquid phase transition, leaving the moisture behavior of chloride salts near their melting point poorly understood. In this study, we investigate how the thermodynamic preference for moisture uptake or release evolves as chloride salts transition from the solid to the liquid state, and examine the consequences of this behavior for the corrosion of a structural alloy.

2. Methods and Results

Six chloride salts were selected to probe moisture behavior across the solid-to-liquid phase transition. The salts were held under a controlled, nominally inert argon atmosphere, and their moisture content was analyzed experimentally as temperature was raised through the melting point. To complement the experimental measurements, neural network interatomic potential (NNIP)-based molecular dynamics simulations were performed to elucidate the underlying thermodynamic origin of the observed behavior. These simulations enabled evaluation of the structural and energetic changes associated with moisture uptake and release in both the solid and liquid states. In parallel, corrosion behavior of a structural alloy (SS316H) was

evaluated through immersion testing in molten salt under two atmospheric configurations: an open system, in which the salt remained continuously exposed to trace moisture from the surrounding glovebox atmosphere, and a closed system, in which the salt was isolated from further moisture ingress. Corroded specimens were characterized using surface and cross-sectional scanning electron microscopy (SEM), together with energy-dispersive X-ray spectroscopy (EDS) elemental mapping and corrosion rates were determined from weight-loss measurements.

3. Results and discussion

The experimental measurements reveal a clear reversal in moisture behavior across the melting point. In the solid state, the salts undergo dehydration, with moisture content decreasing as temperature increases, consistent with the conventional understanding of thermally driven moisture removal. As the salts approach and cross the melting point, however, this trend reverses. The moisture content increases despite the continued rise in temperature, indicating a shift in thermodynamic preference from dehydration to rehydration. NNIP-based simulations show that this reversal arises because the molten state is more structurally disordered and entropically stabilized than the solid state. These conditions make it thermodynamically favorable for the salt to absorb moisture. Notably, this rehydration behavior persists even under a nominally inert glovebox atmosphere containing only trace-level moisture, indicating that it is an intrinsic thermodynamic feature of the molten state rather than an artifact of an imperfectly controlled environment. Corrosion testing of SS316H further demonstrates the practical significance of this behavior. In the open system, where the salt remained continuously exposed to ambient trace moisture, corrosion proceeded through combined intergranular attack and localized pitting. In the closed system, where

further moisture ingress was suppressed, corrosion was substantially mitigated and confined to intergranular attack without pitting. These results collectively indicate that continuous atmospheric moisture ingress, sustained by the salt's intrinsic rehydration tendency in the liquid state, is a key driver of accelerated alloy corrosion, and that limiting this ingress is an effective corrosion mitigation strategy even without eliminating trace moisture from the environment entirely.

4. Conclusions

This study identifies a previously overlooked thermodynamic reversal in the moisture behavior of chloride salts, from dehydration in the solid state to rehydration upon melting, and establishes its connection to the corrosion of structural alloys in high-temperature molten salt environments. By combining experimental moisture measurements, NNIP-based thermodynamic simulations, and comparative corrosion testing under open and closed atmospheric conditions, this work demonstrates that rehydration accompanying the phase transition reflects a genuine thermodynamic tendency of the molten salt, rather than an experimental artifact, and that controlling atmospheric moisture ingress after melting is critical for mitigating corrosion of alloys such as SS316H. These findings offer a new perspective for the design of moisture control strategies in molten salt systems intended for nuclear reactor, motivating further investigation into multicomponent salt mixtures and industrially relevant atmospheric conditions.

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