INL/EXT-21-62675-Revision-0

Assessment of thermodynamic stability of sapphire in eutectic molten chloride environment

January 2022

Anugraha Thyagatur, Michael Buric, Dev Chidambaram, Leslie T. Mushongera, Ruchi Gakhar, Pattrick Calderoni

INL/EXT-21-62675-Revision-0

Assessment of thermodynamic stability of sapphire in eutectic molten chloride environment

Anugraha Thyagatur, Michael Buric, Dev Chidambaram, Leslie T. Mushongera,
Ruchi Gakhar, Pattrick Calderoni

January 2022

Idaho National Laboratory
Idaho Falls, Idaho 83415

http://www.inl.gov

Prepared for the
U.S. Department of Energy
Under DOE Idaho Operations Office
Contract DE-AC07-05ID14517

Assessment of Thermodynamic Stability of Sapphire in Eutectic Molten Chloride Environment

Anugraha Thyagatur[1], Ruchi Gakhar[2], Dev Chidambaram[1], Pattrick Calderoni[2], Michael Buric[3], Leslie T Mushongera[1,*]
[1]Department of Materials Science and Engineering, University of Nevada, Reno, Reno, NV, 87557, USA
[2]Idaho National Laboratory, Idaho Falls, Idaho, USA
[3]National Energy Technology Laboratory, Morgantown, West Virginia, USA
**Corresponding author: lmushongera@unr.edu*

Abstract

The continued development of molten salt reactors and concentrated solar power plants requires highly efficient and stable instruments that can efficiently monitor the chemical conditions of the molten salt during long-term operation in both the fuel and coolant/heat transfer fluid loops. Sapphire (Al_2O_3) fibers have shown tremendous potential due to inherent radiation resistance and a broader operational range of temperature. In this work, computational thermodynamic modeling (CALPHAD) using the ThermoCalc software in conjunction with the SGTE (Scientific Group Thermodata Europe) Molten Salts (SALT1) and Pure Substances (Pure5) databases is applied to understand the compatibility of Al_2O_3 fibers with NaCl-$MgCl_2$ eutectic molten salt in the temperature range of 1500 to 2500 K. The thermodynamic calculations show that sapphire fibers are not expected to be stable over the long-term when exposed to molten chloride salts at these temperatures. To improve the stability of these diagnostic fibers in molten salt environments, various pure metallic elements were evaluated as potential cladding materials for Al_2O_3 fibers. Based on the thermodynamic analysis, molybdenum (Mo) and nickel (Ni) could be effective cladding materials to enhance the stability of Al_2O_3 in NaCl-$MgCl_2$ chloride salt molten bath in the desired temperature range. Thus, the presence of Mo and Ni cladding can provide a protective coating against the corrosive molten salts, thus improving the stability of Al_2O_3. Additionally, it is also shown that Al_2O_3 remains stable up to 2400 K in the presence of pre-existing Al_2MgO_4 and Al_2NiO_4 in the eutectic molten chloride bath environment.

Keywords: Sapphire; Phase Stability; Thermodynamic Modeling; Molten Chloride Salts

1. Introduction

Energy production using molten salt reactors (MSRs) and concentrated solar power (CSP) plants offers several advantages, including lower cost and higher operational safety. Some of the newest MSR and CSP designs use molten chloride salts due to their desirable properties, such as relatively low melting points, low viscosities, and lesser effect on structural materials (corrosion) compared to fluoride melts [1–4]. In this aspect, molten chloride salts have been an excellent choice for thermal energy storage material in CSP plants and heat transfer media in nuclear reactors. Regarding raw materials cost, chloride salts, particularly those containing $MgCl_2$, are by far the least expensive [5–9]. These factors have motivated the selection of the binary NaCl-$MgCl_2$ eutectic molten salt system for application in MSRs and CSPs. While several studies have been conducted on the compatibility of NaCl-$MgCl_2$ molten salts and other molten chloride baths, the corrosion behavior in these environments at the desired operating temperatures in MSRs and CSPs between 600 to 1000°C is very complex [10].

The continued development of MSRs and CSPs has also seen the need for highly efficient instruments for tracking the conditions of the molten salts. An essential requirement for such technology is enhanced stability with respect to the corrosive environments offered by MSRs and CSPs, which is challenging for many materials used in sensing technologies [11]. Critical differences in the salt chemistries and operating temperatures of MSRs and CSPs preclude the application of many materials in the sensing systems [12]. The chloride salt baths containing various corrosive species likely have a significant effect on the stability of the sensor materials. Chloride salts such as NaCl and $MgCl_2$ are very important in this regard because their eutectic composition has a low melting point of 600°C. Ding et al. studied the hot corrosion of stainless steel SS 310, Incoloy 800 H, Hastelloy C-276 in molten $MgCl_2$/NaCl/KCl

(60/20/20 mol%) under an inert atmosphere at 700°C [14]. Their study showed that Hastelloy exhibited the highest corrosion resistance among the three.

Existing sensor technologies were not designed for high-temperature molten salts, requiring significant post-market modifications for material compatibility [7,10,15]. Even with such modifications, these sensor instruments are often not able to operate in the high operating temperatures and corrosive species encountered in MSRs and CSPs. Improved devices are required for monitoring the local conditions of molten salts in the fuel and heat transfer systems. Understanding the effect of these variations is critical to developing sensors for monitoring molten salt characteristics, such as composition, temperature, thermal conductivity, to name a few, in advanced energy production systems. Identifying compatible materials that can be stable in these salt environments and operate at high temperatures is critical to developing such sensors.

Sensors based on silica fibers are attractive because they can be manufactured reasonably. However, silica can also exhibit instabilities at high temperatures, leading to erroneous temperature measurement fluctuation [19,20]. Ceramics of oxide type on the other hand are attractive candidate materials for high temperature applications. Ding et al. studied the mechanical compatibility of ZrO_2 and Al_2O_3 in molten chloride bath of $MgCl_2$-NaCl- KCl mixture at 1000 K [31]. The study showed that ZrO_2 sample surface undergoes structural phase transformation due to reaction with $MgCl_2$. However, no such structural transformation was observed for Al_2O_3. Both Al_2O_3 and ZrO_2 maintained their mechanical compatibility with the molten chloride bath after an exposure period of 600 hours. Nagaoka et al. studied the hot corrosion of alumina (Al_2O_3) and Silicon Carbide (SiC) structural ceramics in a KCl-NaCl molten bath at 700-800°C exposed for 100 to 400 hours [21]. Single-crystal sapphire (Al_2O_3) is chemically inert, offers radiation tolerance, and has a very high melting point (~2050°C) [16]. Therefore, Al_2O_3 fibers could be a suitable candidate for applications in optical fiber-based sensors in high-temperature conditions. Also, single crystal-based sapphire fibers have shown tremendous potential by enabling a broader operational - range of temperature [17–19]. The work demonstrated that while hot corrosion of Al_2O_3 was not observed, SiO_2 emerged as a corrosion product in the case of SiC. However, to our best knowledge, there is a lack of investigation on the corrosion resistance of sapphire fibers exposed to corrosive molten chlorides at temperatures above 800 °C. This study discusses the effect of the molten salt bath environment (NaCl- $MgCl_2$), especially the hot corrosion modeling of clad and unclad sapphire.

The hot corrosion phenomenon indicates material degradation in the presence of molten salts. Previous studies have primarily been based on experimental work. A detailed study of the hot corrosion process was recently reported by Olson et al. [22], who studied the hot corrosion of Hastelloy-N, Haynes-230, Inconel-617, and a C/Si SiC ceramic in FliNaK (LiF-NaF-KF) at 850°C after an exposure time of 500 hrs. The researchers reported de-alloying of Cr from Cr-bearing alloys when exposed to the molten salt bath. Another study by Koger and Litman [23] reported on the stability of Hastelloy-N and Haynes alloy in a sodium fluoroborate mixture. It concluded that in the temperature range of 460 to 605°C, Haynes 25 alloy was damaged by selective leaching of Co and Cr after exposure of 3660 hours.

The high temperature and aggressive nature of molten baths make experimental work quite time-consuming for screening and selection of candidate materials. Computational efforts can significantly lower that time requirement.

Computational frameworks such as CALPHAD (Computer Coupling of Phase Diagrams and Thermochemistry) modeling and ab initio molecular dynamics (AIMD) frameworks have been established to assess the thermodynamic stability and surface reactions of materials in the molten salt environment. Recently, Glazoff et al. [8,24] studied the thermodynamic stability of Alloy 242 and Alloy N in a molten eutectic fluoride environment using CALPHAD modeling. The thermodynamic simulations give an idea of the phases that exist at equilibrium but do not show the reaction pathways. On the other hand, Kwon et al. [25] have extensively used the ab-initio molecular dynamics (AIMD) computational approach to obtain thermodynamic and kinetic properties like diffusion coefficients and the viscosity of LiCl-KCl eutectic molten salt bath mixture with Uranium. The authors developed a model for reliably predicting the effect of LiCl-KCl molten salt on a tungsten (W) electrode for an electrorefining process. The AIMD simulations allow for the analysis of reaction pathways during hot corrosion [26]. However, these simulations are computationally expensive, even considering only a few dozen atoms.

The focus of this work is to assess whether Al_2O_3 fibers could be potentially utilized for critical corrosion components in NaCl-$MgCl_2$ eutectic molten salt environments in temperatures ranging from 600 to 1000°C. For this purpose, computational (CALPHAD) modeling using the ThermoCalc software in conjunction with the SGTE Molten Salts (SALT1) and Pure Substances (Pure5) databases is used. The CALPHAD method is used to obtain a consistent description of the phase diagram and the thermodynamic properties so as to reliably predict the set of stable phases. The SALT1 database contained a variety of assessed systems and is suitable for molten salts calculations and can be used in applications such as hot salt corrosion of materials.

2. The NaCl-$MgCl_2$ Binary System

The quasi-binary phase diagram of NaCl-$MgCl_2$ obtained using Thermocalc and SALT1 is shown in Fig. 1. The following assumptions were made in creating the quasi-binary NaCl and $MgCl_2$ phase diagram using ThermoCalc as discussed in [24]: (1) The phase diagram was not completely assessed with all the intermetallic phases and (2) The molten salt mixture of NaCl and $MgCl_2$ was assumed to be described using the ideal solution model. The above-simplified approach provided insights into the hot corrosion of materials in the salt mixture databases where detailed information on thermodynamics properties and phase equilibria are not available. Similar assumptions were made by Glazoff et al. [24] in their CALPHAD analysis of the thermodynamic stability of Alloy 242 and Alloy N in a molten eutectic fluoride environment. As seen from the quasi-binary phase diagram, there is no solubility of $MgCl_2$ in NaCl or vice versa. The nonvariant eutectic transformation takes place at 600°C with a eutectic point at 50 mol% NaCl.

The predicted phase diagram is different from Ref. [12], which showed a eutectic temperature of 475°C at 42mol% NaCl of binary NaCl-$MgCl_2$ predicted using the FactStage software [12]. To study the composition evolution as a function of temperature, a quasi-binary model based on well-established thermodynamic databases were chosen [30]. Currently, such a model can be studied using Calphad simulations which offers efficient algorithms for minimizing the global Gibbs free energy of a system under equilibrium conditions. The difference in the predicted eutectic temperature could be attributed to over-simplification of the simulations based on the ideal solution model and uncertainties in the thermodynamic databases used.

3. Compatibility assessment of Al_2O_3

In general, the stability of materials in aggressive chemical environments depends on the oxidation of material to form protective oxides. However, the protective oxide layer may dissolve under the action of chemical salts or gases, leaving the underlying material more susceptible to corrosion attack. For example, the formation of the Cr_2O_3 layer on the steel surface acts as a protective coating. However, under extremely aggressive conditions, the dissolution of the Cr_2O_3 layer results in corrosion of the steel [27]. Indeed, computational thermodynamic work has explained the above behavior [2]. The authors [2] have previously studied the effects of molten salt (NaCl), sulfur, oxygen, carbon, and nitrogen on the hot corrosion behavior of Cr alloyed steel. The results indicate that Cr_2O_3 remains stable for up to ~1000°C, followed by rapid dissolution. A similar study has been conducted to study the hot corrosion of stainless steel in a KCl-$ZnCl_2$ molten salt bath mixture [15,28]. These studies show the feasibility of using computational modeling techniques to study the hot corrosion processes of materials in molten salts. While the hot corrosion of steel and other metals has been addressed, the effect of the aggressive chemical environment on ceramics like Al_2O_3 has not been studied for temperatures > 900°C to the best of our knowledge. In this work, an effort has been made to study the hot corrosion of sapphire in NaCl-$MgCl_2$ molten salt bath.

3.1. Al_2O_3 in the molten bath of NaCl-$MgCl_2$Here, we report on the stability of Al_2O_3 in a molten salt bath comprised of NaCl-$MgCl_2$ in the temperature range of 0 to 3000K. The following cases were studied: *(i) Unclad Sapphire (Al_2O_3)* – Pure sapphire in contact with the salt *(ii) Clad Sapphire (Al_2O_3):* - Sapphire and additional cladding metals such as Ni, Au, and Mo in contact with the salt.

3.1.1. Unclad Sapphire (Al_2O_3): The hot corrosion of unclad sapphire in the chloride molten salt mixture is summarized in Fig 2(a). The red line (label-1) represents the mole-fraction of Al_2O_3; the dark blue (label 3 and light blue (label -2) lines indicate $MgCl_2$ and NaCl mole fractions, respectively; the green line (label-4) represents Al_2MgO_4. Other phases include ionic liquid – melting of the NaCl and

$MgCl_2$ eutectic mixture at 750 K: gaseous phase. The instability of the Al_2O_3 manifested in the form of a reduction in its mole fraction. In the temperature range of interest, the Al_2O_3 dissolves to some extent to form Al_2MgO_4. It can also be seen that Al_2O_3 remains relatively stable for up to 1470 K and a relatively considerable conversion to Al_2MgO_4 occurs beyond 1400 K. Although this simulation provided insights into the stability of Al_2O_3, it is not clear if the formed Al_2MgO_4 is protective oxide on the surface or dissolved into the molten salt bath. Thus, based on the thermodynamic calculations, it can be concluded that sapphire fibers may not be compatible with long-term exposure to molten chloride salts at the proposed operating temperature of MSRs.

3.1.2. Clad Sapphire (Al_2O_3): Thermo-Calc modeling is limited in the ability to define the geometry of the system of interest. The effect of cladding on the compatibility of Al_2O_3 can be indirectly assessed by adding the cladding material into the molten chloride bath along with Al_2O_3. This point is relevant to a system in which sapphire fibers are contained in part in a metallic sleeve or coated for part of their length. However, the assumption is that a portion of the fiber is also in contact with the salt (for example, the active sensing length or the fiber termination). The effect of cladding on the thermodynamic stability of Al_2O_3 in NaCl-$MgCl_2$ was examined for various cladding materials, including nickel (Ni), gold (Au), and molybdenum (Mo). The above arrangement is evaluated in Fig. 2(b), which shows the plot of a number of the equilibrium phases in Al_2O_3 with added Ni as cladding material inside the molten chloride bath as a function of the exposure temperature. The red-colored line (label-1) represents Al_2O_3, the brown line (label-2) represents Ni, and the green line (label-3) represents Al_2MgO_4. The simulation results show that in the temperature range of interest, the presence of Ni cladding enhances the stability of the Al_2O_3 as no secondary phases are formed. Furthermore, as seen from Fig. 2(b), Al_2O_3 transforms into Al_2MgO_4 at around 1700K, a higher transition temperature compared to 1470K for an unclad Al_2O_3 (see Fig. 2a). Further, it is assumed that the underlying Al_2O_3 remains stable as long as the cladding material is stable. For example, in Fig 2(b), Ni melts at around 1700 K, and by the above assumption, Al_2O_3 should also be stable up to 1700K.

The plot Fig. 3(a) shows the effect of Au cladding on the stability of Al_2O_3 in the molten chloride bath. The red line (label-1) represents Al_2O_3, the golden line (label-2) represents Au, and the green line (label 3) represents Al_2MgO_4. It can be seen that a small amount of Al_2O_3 transforms into Al_2MgO_4 at around 1700 K. In addition, Au may not be a viable cladding material because it melts at around 1337 K well before the formation of Al_2MgO_4. Fig. 3(b) reveals the effect of Mo cladding on the stability of sapphire in molten chloride bath. As seen from Fig. 3(b), Mo remains stable in its BCC form represented by a green color (label-2) until its melting point of 2400K. Consequently, sapphire should remain stable for up to its melting point of 2400 K. The simulations for metal 'clad' sapphire indicate that the presence of a metallic element (Ni, Au, or Mo) in addition to sapphire leads to the suppression of aluminum dissolution from the sapphire material, thus improving its stability in chloride salts. Mo remains stable in its BCC form represented by a green color (label-2) until its melting point of 2400K. It has been suggested that the addition of a magnesium aluminate (Al_2MgO_4) layer via sol-gel deposition during the fabrication of Al_2O_3 fibers could improve their stability in various environments [29]. Therefore, it was interesting to understand the role of Al_2MgO_4 additions on the stability of Al_2O_3 in the presence of chloride salt. So, the CALPHAD modeling runs were performed for unclad and Ni-clad sapphire with the addition of Al_2MgO_4. The above situation is depicted in Fig. 4(a), which shows that when the weight fraction of Mg is low (not sufficient for eutectic reaction between NaCl and $MgCl_2$), $MgCl_2$ is completely transformed to Al_2MgO_4. Hence the effect of pre-existing Al_2MgO_4 on the compatibility of sapphire in the molten chloride bath was investigated in the NaCl bath in section 3.2.

3.2. Al_2O_3 in the molten bath of NaCl and Al_2MgO_4

3.2.1 Unclad Sapphire (Al_2O_3): As mentioned above, the CALPHAD system could not be initialized with both Al_2O_3 and Al_2MgO_4 as components. Instead, the individual elements such as Al, Mg, and O, along with Na and Cl, were added to the system. In this case, all the Mg added was consumed in the formation of Al_2MgO_4 with no trace of $MgCl_2$, indicating the Al_2MgO_4 precedence over $MgCl_2$ formation. In Fig. 4, the red line (label-1) represents Al_2O_3, the green line (label-2) indicates Al_2MgO_4, the light blue line (label-3) represents NaCl. It can be inferred that Al_2O_3 remains stable in the absence of $MgCl_2$ up to its melting point of 2400 K. The above analysis indicates that the conversion of Al_2O_3 into Al_2MgO_4 occurs primarily because of the presence of $MgCl_2$. The effect of pre-existing Al_2MgO_4 on the stability of Ni cladded sapphire was also investigated in the NaCl bath in the desired temperature range.

3.2.2. Ni-Clad Al_2O_3 in molten NaCl and Al_2MgO_4: In Fig. 5(a), the stability of Ni cladded sapphire was depicted in the presence of Al_2MgO in the NaCl molten bath. The red line (label-1) denotes Al_2O_3, the green line (label -2) represents Al_2MgO_4, and the dark blue line (label-3) indicates Al_2NiO_4. As seen in Fig. 5(a), Al_2O_3 was observed to transform into Al_2NiO_4 at 600 K when the mass of Ni in the NaCl molten bath was 2g (Fig. 5a). This result points to the conversion of Al_2O_3 into Al_2NiO_4, causing instability in the sapphire (Al_2O_3). Interestingly, when the mass of Ni was increased to 20g, as shown in Fig. 5(b), Al_2NiO_4 (dark blue line -label -3) forms at room temperature along with elemental Ni. Al_2O_3 remains stable up to its melting point of 2400 K in the presence of pre-existing Al_2NiO_4 and Al_2MgO_4 in the molten chloride bath, as shown in Fig. 5(b). The above analysis indicates that the addition of Al_2NiO_4 and Al_2MgO_4 may increase the stability of Al_2O_3 in the molten chloride bath.

4. Conclusions

By employing fundamental CALPHAD analysis, it was found that Mo and Ni could be effective cladding or coating materials to enhance the stability of Al_2O_3 in an NaCl and $MgCl_2$ chloride molten salt bath in the temperature range desired for MSR operation. The presence of metallic cladding leads to the suppression of aluminum dissolution from Al_2O_3, thus improving its stability in chloride salts. It was also shown that Al_2O_3 remains stable up to its melting point (2400K) in the presence of pre-existing Al_2MgO_4 and Al_2NiO_4 in the NaCl molten bath environment. The CALPHAD approach used in this work does not predict kinetics or reaction rates. For this purpose, an ab-initio molecular dynamics study is needed to completely understand the dynamics of sapphire or other materials in a chemically aggressive molten salt bath. Furthermore, the effective degradation of the material and its impact on the optical fiber sensor's performance needs to be verified experimentally.

CRediT author statement

Anugraha Thyagatur: Methodology, Investigation, and Writing - Original Draft; **Ruchi Gakhar, Dev Chidambaram, Pattrick Calderoni, and Michael Buric:** Writing - Review & Editing; **Leslie T Mushongera:** Conceptualization, Data verification, Writing - Review & Editing, and Funding acquisition.

Acknowledgments

This work was done under a subaward from Idaho National Laboratory to the University of Nevada, Reno. This work was supported in part by the U.S. Department of Energy, Advanced Research Projects Agency-Energy (ARPA-E) program under project 18/CJ000/06/01.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] M.S. Sohal, P. Sabharwall, P. Calderoni, A. K. Wertsching, B. S. Grover, and P. Sharpe, Conceptual Design of Forced Convection Molten Salt Heat Transfer Testing Loop, September 2010, External Report INL-10-19908 (September 2010)

[2] P. Shi, A. Engstrom, and B. Sundman, 2008, "ThermoCalc Calculations for Materials in Corrosive Environments," SINTEF Symposium, Trondheim, Norway (May 2008)., (n.d.).

[3] S. Phogikaroon, "Molten Salt Technology," University of Idaho (January 2011)., (n.d.).

[4] P.Sabharwall, H. Schmutz, C. Stoots, and G. Griffith, "Tritium Permeation in High-Temperature Reactors," Proceedings of the ASME 2013 Summer Heat Transfer Conference, 2013, (n.d.).

[5] G. Hatem, F. Tabaries, and F. Gaune-Escard, Enthalpies de formation des melanges liquides ZrF4-MF (M = Li, Na, K, Rb), Thermochimica Acta, vol. 149, pp.15-26 (1989), (n.d.).

[6] R.E. Thoma (Editor), Phase Diagrams of Nuclear Reactor Materials, Oak Ridge National Laboratory, ORNL-2542, November 20, 1959.

[7] R.E. Thoma and W.R. Grimes, Phase Equilibrium Diagrams For Fused Salt Systems, ORNL Chemistry Division, Technical Report # W-7485-eng-26, June 24 1957. Based on: ANI Quarterly Progress Report June 10, 1952, ORNL-1294, p.91, (n.d.).

[8] M. V. Glazoff, A. Tokuhiro, S.N.Rashkeev, and P. Sabharwall, Zirconium, Zircaloy-2, and Zircaloy-4: Computational Thermodynamics and Atomistic Perspective on Hydrogen Uptake and Oxidation, Journal of Nuclear Materials, vo.444, pp.65-75 (2014), (n.d.).

[9] D. A. Shores, "New Perspectives on Hot Corrosion Mechanisms," Proc. Intl. Conf. on High-Temperature Corrosion, Ed., R. A. Rapp, N. A. C. E., Houston, p. 493 (1983).

[10] A.G. Fernández, L.F. Cabeza, Corrosion evaluation of eutectic chloride molten salt for new generation of CSP plants. Part 1: Thermal treatment assessment, J. Energy Storage. 27 (2020) 101125. https://doi.org/10.1016/j.est.2019.101125.

[11] R. Sanga, S. Agarwal, M. Sivaramakrishna, G.P. Rao, Deployment of quasi-digital sensor for high temperature molten salt level measurement in pyroprocessing plants, Rev. Sci. Instrum. 89 (2018) 045007. https://doi.org/10.1063/1.5012803.

[12] FACTSTAGE, "FSalt Thermodynamic Database for Molten Salt Applications" (2011)., (n.d.).

[13] O. Benes, Thermodynamics of Molten Salts for Nuclear Applications, Ph.D. Dissertation, Advisors: Dr. David Sedmidubský, and Dr. Rudy J. M. Konings, Prague (2008).

[14] W. Ding, H. Shi, Y. Xiu, A. Bonk, A. Weisenburger, A. Jianu, T. Bauer, Hot corrosion behavior of commercial alloys in thermal energy storage material of molten MgCl2/KCl/NaCl under inert atmosphere, Sol. Energy Mater. Sol. Cells. 184 (2018) 22–30. https://doi.org/10.1016/j.solmat.2018.04.025.

[15] H. E. McCoy, Jr., Status of Materials Development for Molten Salt Reactors, ORNL/TM-5920 (January 1978), (n.d.).

[16] Islamov et al., "Radiation-optical characteristics of quartz glass and sapphire," J

Nucl. Mater, 2007, (n.d.).

[17] W.T. Spratt, M. Huang, C. Jia, L. Wang, V.K. Kamineni, A.C. Diebold, H. Xia, Formation of optical barriers with excellent thermal stability in single-crystal sapphire by hydrogen ion implantation and thermal annealing, Appl. Phys. Lett. 99 (2011) 111909. https://doi.org/10.1063/1.3637613.

[18] R.K. Nubling, R.L. Kozodoy, J.A. Harrington, Optical properties of clad and unclad sapphire fiber, in: J.A. Harrington, D.M. Harris, A. Katzir, F.P. Milanovich (Eds.), Los Angeles, CA, 1994: p. 56. https://doi.org/10.1117/12.180738.

[19] H. Chen, M. Buric, P.R. Ohodnicki, J. Nakano, B. Liu, B.T. Chorpening, Review, and perspective: Sapphire optical fiber cladding development for harsh environment sensing, Appl. Phys. Rev. 5 (2018) 011102. https://doi.org/10.1063/1.5010184.

[20] D. Grobnic, C. W. Smelser, S. J. Mihailov, and R. B. Walker, “Longterm thermal stability tests at 1000 °C of silica fibre Bragg gratings made with ultrafast laser radiation,” Meas. Sci. Technol., vol. 17, no. 5, pp. 1009–1013, 2006.

[21] T. Nagaoka, K. ichiro Kita, N. Kondo, Hot corrosion of Al_2O_3 and SiC ceramics by KCl & NaCl molten salt, J. Ceram. Soc. Jpn. 123 (2015) 685–689. https://doi.org/10.2109/jcersj2.123.685.

[22] L. C. Olson, “Materials Corrosion in Molten LiF-NaF-KF Eutectic Salt,” Ph.D. Dissertation (Advisor – Prof. T. R. Allen) University of Wisconsin-Madison (2009)., (n.d.).

[23] J. W. Koger, and A. P. Litman, “Mass Transfer between Hastelloy N and Haynes Alloy 25 in a Molten Sodium Fluroborate Mixture,” ORNL-’I’M-3488 (October 1971).

[24] Glazoff, M. V. “Thermodynamic Assessment of Hot Corrosion Mechanisms of Superalloys Hastelloy N and Haynes 242 in Eutectic Mixture of Molten Salts KF and ZrF4.” (2012)., (n.d.).

[25] C. Kwon, J. Kang, W. Kang, D. Kwak, B. Han, First principles study of the thermodynamic and kinetic properties of U in an electrorefining system using molybdenum cathode and LiCl-KCl eutectic molten salt, Electrochim. Acta. 195 (2016) 216–222. doi:10.1016/j.electacta.2016.02.123,

[26] H. Wang, E.-H. Han, Ab initio molecular dynamics simulation on interfacial reaction behavior of Fe-Cr-Ni stainless steel in high temperature water, Comput. Mater. Sci. 149 (2018) 143–152. doi.org/10.1016/j.commatsci.2018.03.025.

[27] R. Bradshaw, S. Goods, Corrosion of Alloys and Metals by Molten Nitrates, 2001. https://doi.org/10.2172/1545803.

[28] H. E. McCoy, Jr., 1971, “An Evaluation of The Molten-Salt Reactor Experiment Hastelloy N Surveillance Specimens - Fourth Group,” ORNL/TM-3063 (March 1971).

[29] S. Bera, B. Liu, J.K. Wuenschell, J. Baltrus, D. Lau, B. Howard, M.P. Buric, B.T. Chorpening, P.R. Ohodnicki, Fabrication, and evaluation of sapphire fiber cladding via magnesium aluminate spinel sol-gel based approaches, in: G.A. Sanders, R.A. Lieberman, I.U. Scheel (Eds.), Fiber Opt. Sens. Appl. XVI, SPIE, Baltimore, United States, 2019: p. 19. https://doi.org/10.1117/12.2518506.

[30] O. Beneš, R.J.M. Konings (2008). Thermodynamic evaluation of the NaCl–MgC_{l2}–UCl_3–$PuCl_3$ system. , 375(2), 202–208. doi:10.1016/j.jnucmat.2008.01.007

[31] Ding, W.; Shi, Y.; Braun, M.; Kessel, F.; Frieß, M.; Bonk, A.; Bauer, T. Compatibility of 3D-Printed Oxide Ceramics with Molten Chloride Salts for High-Temperature Thermal Energy Storage in Next-Generation CSP Plants. *Energies* **2021**, *14*, 2599. https://doi.org/10.3390/en14092599

Caption Table

Figure 1. Quasi binary approximation of molten chloride phase diagram of $MgCl_2$ and NaCl from calculations using Thermocalc software. The composition and temperature of interest is the eutectic point with 50 mol% NaCl and temperature of 600 °C.

Figure 2. Moles of thermodynamically stable phases obtained upon exposure of (a) unclad sapphire (Al_2O_3) and (b) Ni-clad sapphire to NaCl-$MgCl_2$ salt-mixture, at temperatures ranging from 200-3000 K.

Figure 3. Moles of thermodynamically stable phases obtained upon exposure of (a) Au-clad sapphire (b) Mo-clad sapphire, to NaCl-$MgCl_2$ salt-mixture, at temperatures ranging from 200-3000K.

Figure 4. Moles of thermodynamically stable phases obtained upon exposure of unclad sapphire (Al_2O_3) to NaCl salt, at temperatures ranging from 200-3000K, in presence of Al_2MgO_4 phase in the initial system.

Figure 5. (a) Al_2O_3 was observed to transform into Al_2NiO_4 at 600 K when the mass of (Ni) = 2g in the NaCl molten bath environment, however increasing the Ni content to 20 g (b) Al_2NiO_4 was formed at ambient conditions before the beginning of the simulation. This plot indicates that in the presence of pre-existing Al_2MgO_4 and Al_2NiO_4, Al_2O_3 remains stable up to its melting point 2300 K in NaCl molten bath environment.