Wetting of Graphite by Molten Fluoride Salts: Initial Experiments

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INTRODUCTION

There is growing global interest in developing advanced nuclear reactors; they are a promising component of a sustainable energy future due to their economic competitiveness with other energy sources, passive safety features, non-polluting operation, and nuclear proliferation resistance. Many advanced reactor concepts use molten salt coolant to enable higher operating temperatures, which increases thermal efficiency. The Fluoride-Salt-Cooled High-Temperature Reactor (FHR) is an under-development advanced reactor that is cooled with Li_2BeF_4 salt (FLiBe). The FHR is especially attractive among other advanced reactors because it is designed to be readily commercialized due to features such as compatibility with commercially available turbines[1]. One of the major barriers to licensing and commercializing the FHR is understanding properties of FLiBe that enable prediction of the reactor's behavior in normal operation and in accident scenarios.

It is of interest to characterize the wetting properties of FLiBe on the graphite surfaces of FHR pebble fuel elements. Wettability affects salt penetration into porous graphite[2], which could inhibit its structural integrity and ability to absorb tritium in the FHR core (tritium is a product of FLiBe irradiation). Wetting can also impact heat transfer and flow; in nonwetting systems, gas can become trapped between the solid and liquid interface and form a film[3].

Surface wettability is determined by the contact angle at the three-phase (liquid-solid-gas) boundary, which is typically measured from a photograph of a sessile droplet with image processing techniques. The sessile drop method is shown in Fig. 1; a liquid exhibits high wetting when the contact angle is less than 90° and low wetting when the contact angle is greater than 90°[4].

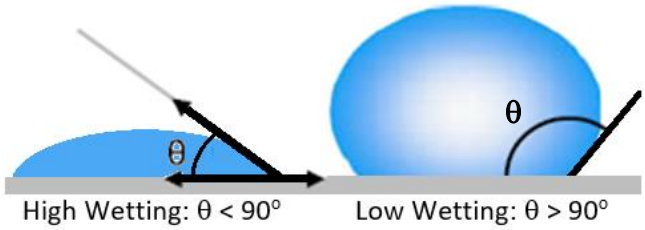

Figure 1: Contact angle measurements from sessile drops.

When a liquid first contacts a surface, its contact angle changes until it reaches equilibrium (when the surface free energy is minimized). Wettability strongly depends on the surface profile of the solid[5][6]. Surface defects such as grain boundaries, scratches, or pores can inhibit the advancing and receding of the contact angle and change the equilibrium configuration. Wettability also depends on surface chemistry[5]; chemical reactions between the gas, liquid, and solid can cause the wetting characteristics to vary or exhibit time-dependence.

FHR performance could be affected if FLiBe-graphite wetting is dynamic during operation due to graphite surface damage or salt composition changes from impurities. This study and future work aim to elucidate the dependence of FLiBe-graphite wetting on surface profile and interface chemistry by presenting initial experimental results and comparing them to prior studies of salt-graphite wetting.

MSRE Wetting Studies

In the 1960s, the wetting properties of molten fluoride salts on nuclear graphite grade CGB were investigated at Oak Ridge National Laboratory (ORNL) during the Molten Salt Reactor Experiment (MSRE). The MSRE study found that FLiBe-graphite wetting strongly depends on moisture content. In sufficiently dry helium, FLiBe did not wet graphite, but as low as 10 ppm of H_2O vapor caused total wetting, as shown in Fig. 2, and an oxide scum to form on the FLiBe droplet[3]. At higher H_2O concentrations, the oxide scum on FLiBe became rigid and prevented contact angle change. Sensitivity to water vapor is likely due to reactions between H_2O and BeF_2, which is supported by experiments with non-beryllium salts that observed stagnant contact angles in high H_2O concentrations. For example, the contact angle of LiF-NaF-KF salt, (FLiNaK) on CGB remained constant as water vapor was added to dry helium up to 200 ppm[3]. Furthermore, unlike water vapor, the FLiBe-graphite contact angle was not sensitive to O_2; it remained constant at O_2 levels of up to 400 ppm in helium[7]. The MSRE study found that FLiBe-graphite contact angle did not exhibit temperature dependence in range of approximately 500 to 800°C.

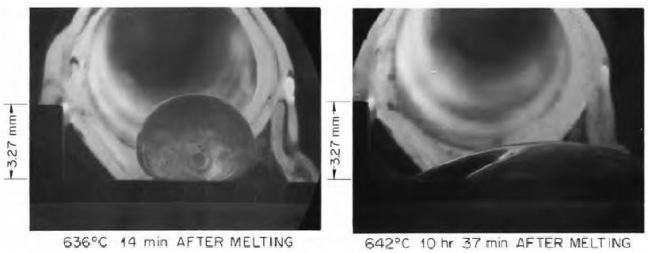

Figure 2: FLiBe is non-wetting on graphite in dry helium (left) but wets graphite at 10 ppm H_2O in helium (right)[3].

EXPERIMENTAL SETUP

In the present study, the contact angle of molten fluoride salts, FLiBe and FLiNaK, was measured on nuclear graphite IG-110 and matrix graphite A3 over a range of temperatures using the sessile drop method. FLiBe was selected for its relevance to the FHR, and FLiNaK was studied because it is a common simulant salt for FLiBe in thermal-hydraulic experiments. The FLiBe (LiF-BeF_2, 67-33 mol%) salt was produced from raw components and purified with Ar and H_2/HF bubbling at the University of Wisconsin (UW)-Madison[8]. The FLiNaK (LiF-NaF-KF, 46.5-11.5-42 mol%) was also produced at UW-Madison. IG-110 and A3 are graphite types of interest for advanced high-temperature nuclear reactors[9][10].

Pieces of solid salt (shown in Fig. 3) were heated using a furnace from room temperature on graphite samples, and at their melting points the salts contracted to form droplets. The samples were heated inside a glovebox, which protects laboratory personnel from beryllium hazards and maintains an argon atmosphere with H_2O and O_2 levels below 4 ppm to avoid salt contamination. Graphite samples were baked at 700°C for three hours prior to experiments to remove moisture. The graphite samples were positioned on a copper block to improve heat conduction from the furnace to the salts. A thermally insulating ½" thick calcium-silicate lid (shown in Fig. 3) was placed over the samples, which had a ceramic glass window, rated for 700°C, through which the droplets were photographed. A thermocouple on the copper monitored the temperature. Once the experiment reached a temperature of interest, the droplets were photographed with a digital camera through the lid and glovebox windows. The glovebox window is rated for 120°C; an additional thermocouple on the window ensured that it was not overheated. All contact angle measurements were made using DataPhysics SCA 20 contact angle software[11].

Figure 3: Solid FLiBe and FLiNaK samples on nuclear graphite, on a copper block, above a furnace. The insulating calcium-silicate lid is displayed behind the samples.

RESULTS

The results of the contact angle measurements for six FLiBe samples (S1-S6) and four FLiNaK samples (S7-S10) on A3 and IG-110 are shown in Fig. 4. The droplets were not axisymmetric, so contact angles on each side of the droplet were measured independently. The vertical error bars represent the range of repeated measurements; error is mainly due to manual boundary selection in SCA 20. The horizontal error bars represent the temperature range of repeated measurements and do not account for thermal uncertainties within the setup.

The MSRE literature reports that the FLiBe contact angle on CGB is 147 ± 12° at 500 to 800°C, and that of FLiNaK is 90 ± 4° at 500 to 720°C[3]. Fig. 4 shows how the MSRE contact angle data compares to the data in this study. Most of the FLiNaK data varies significantly from the MSRE data; however, they more closely agree with recent wetting studies that determined the contact angle to be about 135° for FLiNaK on nuclear graphite[6].

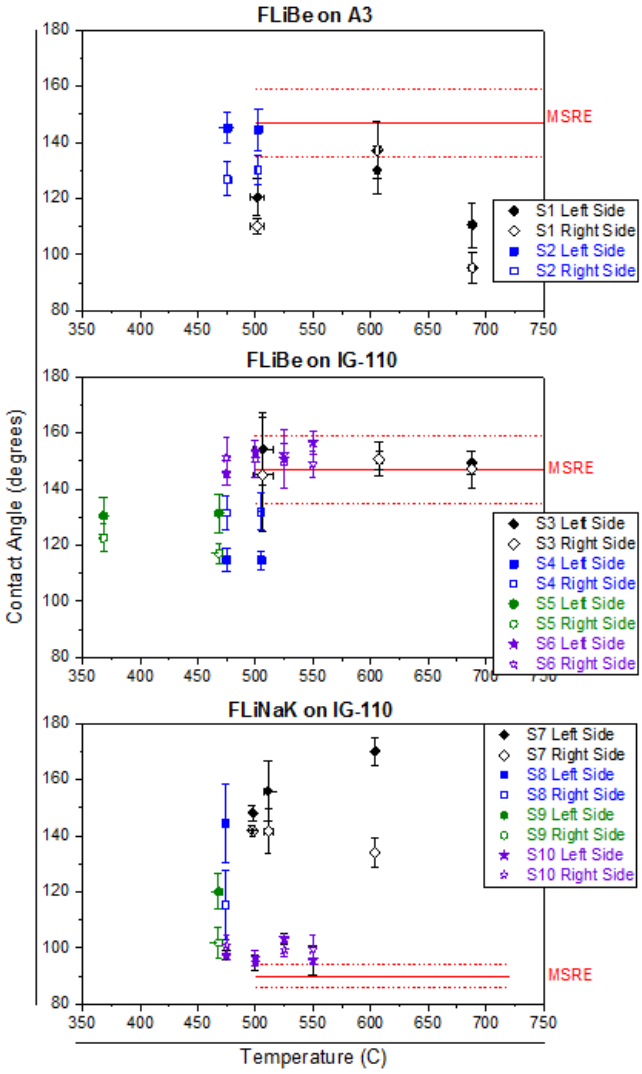

Figure 4: FLiBe and FLiNaK contact angle on graphite.

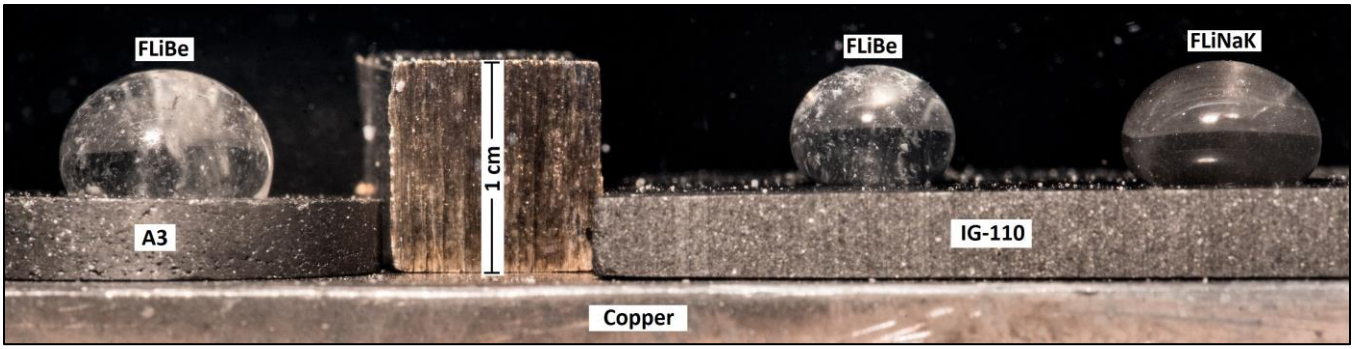

Figure 5: FLiBe and FLiNaK sessile droplets at 500ºC on matrix graphite A3 and nuclear graphite IG-110 at UW-Madison.

For a given salt type, graphite type, and temperature, contact angle measurements exhibited a wide range of values, indicating that the experiments have poor repeatability. For a given temperature, FLiBe samples exhibited contact angles that varied by as much as 35º on A3, and by as much as 40º on IG-110. FLiNaK samples exhibited contact angles that varied by as much as 44º on IG-110. Droplets also exhibited a large discrepancy in contact angle on either side of the same droplet. This effect is evident in the FLiBe droplet on A3 shown in Fig. 5. Among all the FLiBe measurements, the contact angles on different sides of the same droplet varied by as much as much as 18º, and by as much as much as 36º for FLiNaK. One reason that the contact angle measurements exhibited poor repeatability could be due to variations on the surface profile of the graphite. On an ideally smooth surface, the contact angle would be the same on both sides of the droplet. The graphite samples in this study were mechanically polished and appeared smooth, but microscopic details, such as scratches from polishing, pores, or structures from graphite manufacturing processes, could have been present that affected the contact angle. A closer look at the graphite surface profile elucidates what types of features are to be expected in the samples on micron to nanometer scales.

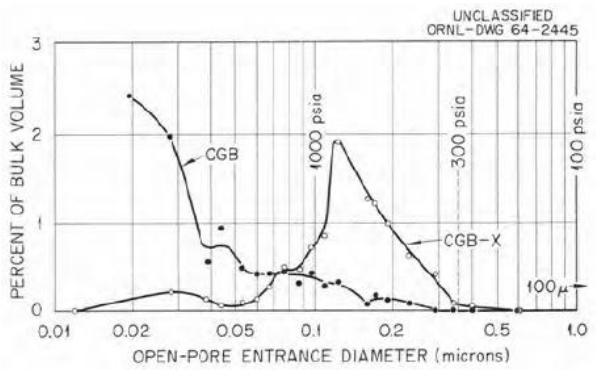

Figure 6: CGB Porosimetry studies from MSRE[12].

Studies from MSRE report that most surface-accessible pores of CGB are below 0.4 microns in diameter; the majority are on the order of tens of nanometers, as shown in Fig. 6, and that CGB has a porosity of about 18%[12]. Studies of IG-110 report that its porosity is about 15%, and that most of the pore volume is comprised of tiny pores[9], much like CGB. Another study involving matrix graphite A3 reports a bimodal pore distribution, and an average pore diameter on the order of microns[10]. Differences in porosity could cause differences in wettability; similarities between FLiBe contact angle on CGB and IG-110 could indicate that nanoscale pores have a significant impact on wetting properties.

A photomicrograph of CGB from the MSRE is shown in Fig. 7[12], which shows its main constituent, graphitized coke particles, and the binder material. The white spots are non-porous solid material from impregnations and heat treatments during manufacturing. A3 and IG-110 are made with distinct raw materials, pressing processes, and heat treatments; therefore, they have distinct structures and properties. For example, A3 has been observed to have different oxidation behavior than nuclear graphite[10]. Differences in surface profile of A3 and IG-110 are visible with SEM studies done at UW, but it is unclear how they affect wetting. This is an area of future study.

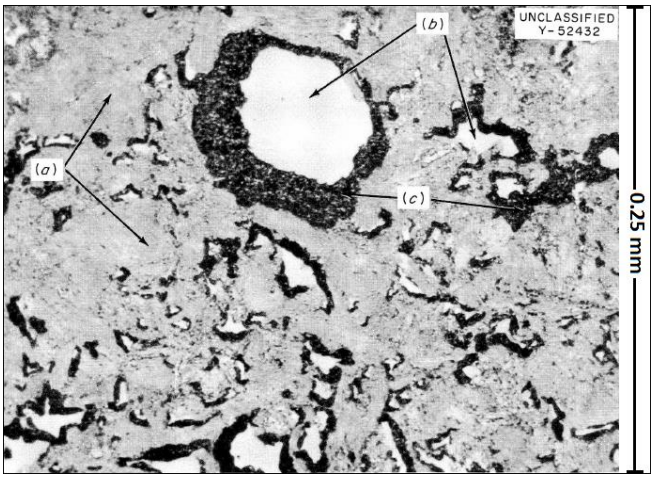

Figure 7: Microstructural details of CGB from MSRE. (a) *graphitized coke particles. (b) and (c) structures developed through impregnations and heat treatments[12].*

Contact angle was not clearly observed to depend on temperature, which is consistent with [2] and [3]. Deviations

in contact angle over a range of temperatures were mostly within the uncertainties of the measurements in that range.

Moisture in the graphite likely contributed to the spread in the contact angle data. The sensitivity of FLiBe to moisture is reported in MSRE literature; oxide scum formed at the FLiBe-gas interface due to water vapor reacting with BeF_2[3]. Furthermore, initial contact angle experiments at UW, prior to this study, showed that FLiBe wet unbaked graphite. Though the graphite in this study was baked to remove moisture, there is evidence that moisture still may have been present. Videos of droplets melting show particles circulating within FLiBe droplets. It is possible that the particles are oxide scum from the FLiBe-graphite interface. This would also explain why particles were not observed circulating in FLiNaK, since it does not contain BeF_2.

Droplet size can also affect contact angle[4], which adds challenges to conducting repeatable sessile drop experiments. The MSRE literature does not report extensively on droplet size, but Fig. 2 gives an idea of their scale. Most drops in this study were similarly sized to those in Fig. 2, though some were larger by as much as 4 mm in width. A clear dependence of contact angle on droplet size was not observed in this study but will be incorporated into future work.

Though the droplets did not visibly change in dimension, they may have changed in composition due to evaporation during heating and oxide formation. Composition change likely depends on experiment duration and maximum temperature, but controlled experiments are needed to understand this dependence and how it affects wetting.

CONCLUSIONS AND FUTURE WORK

FLiBe and FLiNaK exhibited low wetting on graphite in dry argon, which is consistent with the MSRE studies[3]; however, there was a large spread in the contact angle data. Contact angle measurements exhibit poor repeatability because the wettability of a solid is highly sensitive to its surface profile, mechanical and chemical interactions with the liquid, and the ambient conditions[5].

The data suggest that differences in FLiBe and FLiNaK contact angle with the three types of graphite; A3, IG-110, and CGB; could be attributed to differences in porosity and structure. Further study of graphite surface profile using SEM and atomic force microscopy could elucidate the extent of this dependence, and whether polishing impacts the contact angle measurements.

Further studies are underway at UW on the impact of graphite moisture content and surface profile on wetting properties. A computer program is under development that automates contact angle measurements using edge-detection image processing techniques. Scripted measurements will reduce error from boundary selection and increase data processing efficiency.

ACKNOWLEDGEMENTS

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