INL/CON-05-00927
PREPRINT

Beryllium Interactions In Molten Flibe

Twelfth International Conference on Fusion Reactor Materials

G. R. Smolik
M. F. Simpson
P. J. Pinhero
M. Hara
Y. Hatano
R. A. Anderl
J. P. Sharpe
T. Terai
S. Tanaka
D. A. Petti
D. K. Sze

January 2006

Beryllium Interactions in Molten Flibe

G. R. Smolik[1], M. F. Simpson[1], P. J. Pinhero[1], M. Hara[2], Y. Hatano[2], R. A. Anderl[1],
J. P. Sharpe[1], T. Terai[3], S. Tanaka[3] and D. A. Petti[1], D.-K. Sze[4]

[1]Idaho National Laboratory, P.O. Box 1625, Idaho Falls, Idaho 83415, USA
[2] Hydrogen Isotope Research Center, Toyama U., Gofuku 3190, Toyama 930-8555, Japan
[3]The University of Tokyo, Hongo 7-3-1, Bunkyo-ku, Tokyo 113-8656, Japan
[4]University of California at San Diego, San Diego, CA, USA

Abstract

Molten flibe ($2LiF\cdot BeF_2$) is a candidate as a cooling and tritium breeding media for future fusion power plants. Neutron interactions with the salt will produce tritium and release excess free fluorine ions. Beryllium metal has been demonstrated as an effective redox control agent to prevent free fluorine, or HF species, from reacting with structural metal components. The extent and rate of beryllium solubility in a pot design experiments to suppress continuously supplied hydrogen fluoride gas has been measured and modeled[1]. This paper presents evidence of beryllium loss from specimens, a dependence of the loss upon bi-metal coupling, i.e., galvanic effect, and the partitioning of the beryllium to the salt and container materials. Various post-test investigative methods, viz., scanning electron microscopy (SEM), Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS) were used to explore this behavior.

1. Introduction

The 2:1 mol% mixture of LiF and BeF_2 had been used for the coolant and fuel salts in the Molten Salt Research Program during the 1960-70s. They reported that beryllium metal was used to maintain high U^{+4} to U^{+3} ratios thus preventing U reaction with the graphite moderator. The fluorine activity was also lowered preventing reactions with container materials[2]. In fusion applications the production of tritium is higher leading to higher levels of tritiated species of HF. A goal of Task 1-1-A of (JUPITER-II) the Japan/US Program on Fusion Energy Reseach at the INL was to demonstrate that HF in molten flibe could be controlled by the dissolution of Be metal which would act as a redox agent. Our companion paper[1] describes these experiments conducted in a pot design setup using about 0.5 kg of salt. These experiments indicate that Be dissolution increases linearly to near 0.003 mol% Be metal in the flibe for one hour exposures. Uncertainties remain regarding the mechanism of Be uptake into the flibe for these experiments. Greater material losses occurred from Be specimens in close proximity to the nickel fixture or wires (see Fig. 1) suggesting some galvanic influence. Conversely, a test with an alumina fixture to electrically insulate the Be sample did not show the general trend of HF concentration suppression when the Be was immerged. Smaller scale tests were performed in an inert gas glove box to try to determine the solubility limit of Be metal in flibe, to confirm galvanic effects and to examine where the Be becomes redistributed. This paper describes these latter tests and post-test examinations.

2. Experimental methods

Different types of tests were run in the inert gas glove box. One preliminary test involved placing a Be rod (7.6 mm diameter x 6.4 mm long) into 20 g of flibe in a dish-shaped nickel crucible. The depth of the molten flibe was sufficiently low that the Be rod, although less dense than the salt, contacted the bottom of the crucible during the 210 hour exposure at 803K. Helium gas was purged through the headspace above the crucible during the test. Visual appearance indicated that the rod lost about 25 percent of its volume. The sample loss of 0.134 g, assuming distribution into the flibe, represents about 2.4 mol%. The molecular weight of the molten flibe is taken as 33 to remain consistent with earlier notation. Pieces of the salt were then dissolved in 5.8 N H_2SO_4 and released gas collected by an inverted funnel and burette setup. The amount of Be metal potentially present in the salt was then calculated assuming that gas release represented hydrogen from the reaction: $Be^0 + H_2SO_4 \rightarrow BeSO_4 + H_2$ (g). Values obtained from these dissolutions varied between 0.10 and 0.42 mol% Be metal, thus they were much lower than that indicated from the sample loss. Another test was run with slight variations. A longer Be sample (7.6 mm diameter x 30.5 mm long) was vertically suspended into a 10 g batch of flibe contained in a glassy carbon crucible (GCC). This sample showed no indication of attack after the 74 hour exposure but salt dissolutions released similar amounts of gas as the previous test.

Fig. 1. Redox specimen showing non-uniform attack.

A setup designed to test two Be samples simultaneously is shown in Fig. 2. One sample was held in a nickel fixture and suspended into a nickel crucible. The sample and the crucible could be connected to create a galvanic couple. The other sample was held in an alumina fixture to electrically insulate it from the GCC or Ni crucible, and the test vessel. The insulated sample Be5 and the coupled sample Be6 from the first test are shown in Fig. 3. Specimen Be5 shows no evidence of attack whereas Specimen Be6 visibly lost material after 160 hours. A second similar test was run with this setup for 104 hours. The circuitry for measuring the voltage between the Be sample and nickel crucible remained connected thus the galvanic coupling did not exit. As expected neither sample showed any indication of external attack. A third test was run for 150 hours with Specimen Be9 (insulated) and Specimen Be10 (galvanically coupled) both using a Ni crucible. Again, the insulated sample did not while the coupled sample showed evidence of attack (see Fig. 3).

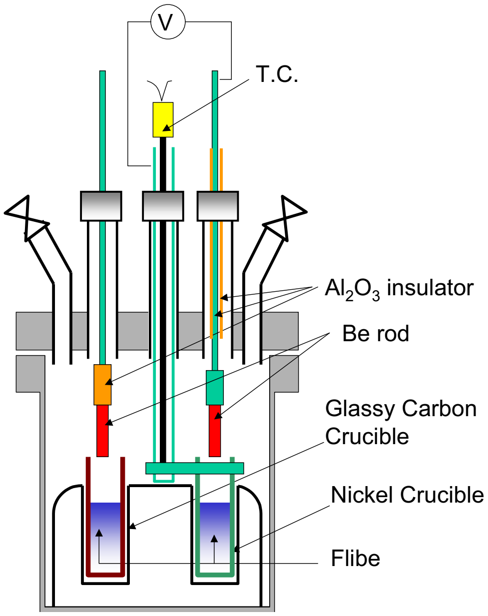

Fig. 2. Setup to test both an electrically insulated and a galvanic coupled Be sample in molten flibe simultaneously.

Samples of salt were removed from the nickel and GCC crucibles. Improved techniques allowed the salt ingot from the Be10 test to be removed generally intact (see Fig. 4). Samples could then be selectively obtained from the outer and internal locations from the ingot. These samples of salt were then subjected to the acid dissolution test described above. Some Be samples were fractured providing views of cross sections as well as outer surfaces. Pieces were cut from nickel crucibles containing Be samples that had undergone significant losses. Samples of the salts, Be samples and crucible were submitted for analyses by SEM, AES and XPS.

Fig. 3. Be Samples Be5, Be6, Be9 and Be10 (left to right) exposed for 150 hours at 530°C in molten flibe.

3. Experimental results and discussion

Edge locations of the Be10 salt ingot shown in Fig. 4 had some dark material and macroscopically apparent shinny grains. Gas released from samples from this region, when dissolved in H_2SO_4 acid, represented 0.20 and 0.34 mol% Be metal in the salt. These values are within the range obtained from the preliminary test. Salt from interior locations had a light whitish appearance and no apparent dark inclusions. Such samples when dissolved released gas representative of only 0.006 and 0.009 mol% Be metal. This is near or only slightly above the estimated detection limit of 0.005 mol%. Center salt from the Be9 test, i.e., the insulated sample, also generated only a minor amount of gas. The projected Be metal concentration was 0.006 mol%. Salt from the bottom surface of the Be9 ingot, although significantly black, released gas only equivalent to 0.011 mol% Be metal in salt. These tests confirm greater gas release from salt containing the galvanic coupled specimen. The greater loss from the galvanic coupled Be sample and relatively small gas generation from the Be9 bottom salt support a correlation of gas generation to Be metal. The Be is shown to concentrate at exterior surfaces. One may question whether segregation occurs during solidification. However, evidence to be provided shows that a significant amount of the Be is transferred and diffused into the Ni crucible. This suggests that the transfer occurs during the long-term exposure and is likely promoted by potential differences from the galvanic coupling.

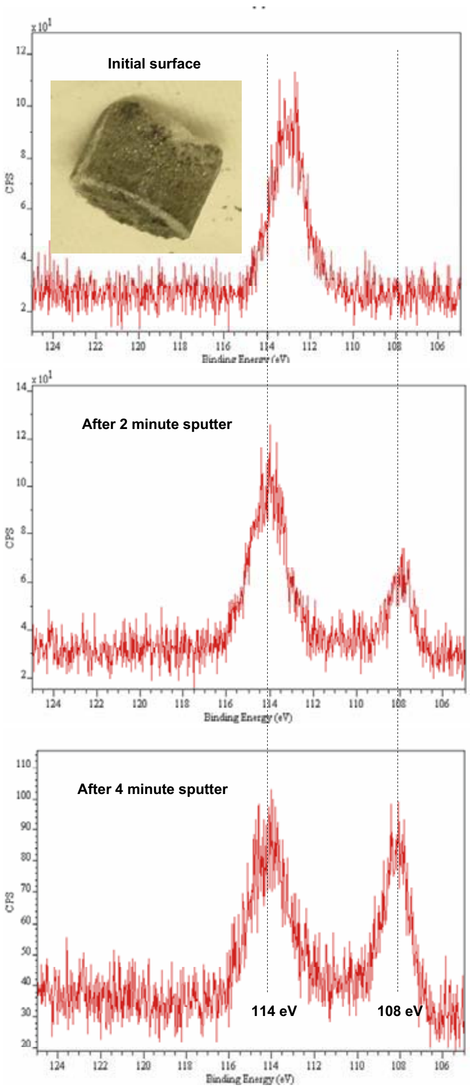

Fig. 4. Be10 salt ingot with XPS spectra showing Be related peaks: Initial surface (top), after 2-minute sputter (center), and after 4-minute sputter (bottom).

A sample of the edge salt from Be10 was examined by XPS. XPS examinations of flibe and BeF_2 crystals are plagued by contamination inherent to surface examinations and charging associated with the ionizing beam. Initial spectra showed a peak, or possible two, overlapping peaks near 113.5 eV. This could represent either, or both, BeF_2 or BeO. Published peaks for BeO and BeF_2 are (113.6 to 114.2 eV) and (115.3 to 116.2 eV), respectively. Analyses of the initial spectra indicated that the Li to Be ratio was below 2, i.e., 1.7 to 1.8, and there was deficient fluorine to accommodate the positive charges of the (Be+Li) anions by a factor of about 0.5. Sputtering to remove O and C surface contamination caused the

Be associated peak to split into one centered near 108 eV and one near 114.2 eV. The published peak for Be metal is 111.8 eV. This implies Be metal may have been present but covered by a thin BeO that was removed by sputtering. The development of the Be metal peak, irregular ratio of Li to Be and deficient fluorine ion, along with macroscopic apparent shinny crystals on the flibe, suggest that Be metal could be present on the outer surface of the Be10 salt. However, we have observed a similar phenomenon upon sputtering pure BeF_2 samples, i.e., the development a second peak indicative of a Be metal at a lower energy. We therefore still consider the above XPS indications as somewhat tenuous proof of Be metal on the flibe surface.

Fracturing Specimens Be6 and Be10 by cantilever beam loading over a knife-edge provided nice flat fractures dislodged some residual scale/salt near the fractures. This revealed how much Be metal remained in the rod. The Be10 shown in Figure 3 had a 5.2-mm initial diameter, a 4.4-mm post-test diameter and 3.4-mm diameter metal core. Thus 0.428 gram of Be was removed or reacted from the specimen. Such uptake of Be metal in the 20 grams of salt would represent 7.8 mol%. This is more than 20 times higher than that estimated from the acid dissolutions from the outer edge salt. The residual scale and the scale:metal interface best revealed by SEM are shown for the Be6 sample in Fig. 5. The Be metal core appears dark when imaged with back scatter electrons. The outer scale appears light. Energy dispersive x-ray analyses (EDS) provided only indications of fluorine from this light phase. Be and Li cannot be detected by this method. Thus spectra showed no signal from the metal core or from the particles embedded into the outer scale. Since no HF was purged into the salt we assume that the outer fluoride bearing scale is residual flibe. Outer scale from a REDOX specimen similar to the one shown in Fig. 1 had been removed and analyzed by inductive coupled plasma – atomic emission spectroscopy (ICP-AES). These measurements indicated a Li to Be mass ratio of only 0.88, the normal ratio in flibe is 1.54. This shift in Li to Be ratio presumably can be attributed to Be metal grains incorporated into the layer of salt. The ICP analyses also indicated that other metals can become concentrated in the scale. These metals included the following in ppm: Al – 930, Cr – 6240, Fe – 9140, Mn – 2320, and Ce- 730. These metal have also been sporadically observed non-uniformly in residual scales on other Be samples by SEM/EDS. These ICP measurements are one to two orders higher than those measured in bulk flibe. This suggests that these elements perhaps become concentrated from impurities inherent either in the salt or in the Be metal. Side views of fractured specimens Be6 and Be10 were examined with AES and XPS. Analyses at thick scale locations provided spectra indicative of the flibe salt. Both methods indicated higher Be content at locations where the scale had spalled to near the specimen interface. AES spectra displayed a peak at 104 eV that correlates with the published value for Be metal. The intensity of this peak increased to reflect a change in Be metal from 12 to 65 at% when sputtered to an estimated depth of 5000 Å. These observations are in general agreement with earlier observations[3] and suggest that the Be metal peaks are associated with Be metal grains incorporated into the salt as revealed by cross sections in Fig. 5.

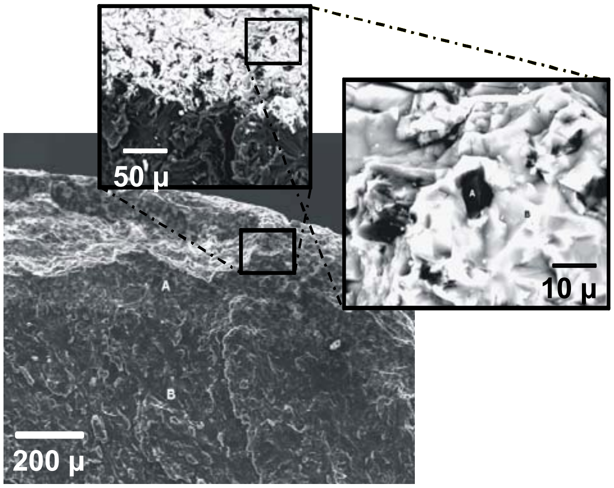

Fig. 5. SEM image of the Be6 at the salt to Be metal interface.

A view of the inner surface of the nickel crucible for the Be6 test is shown in Figure 6. The crucible needed to be deformed to remove the salt. This caused spalling to occur from an apparent embrittled layer extending into the nickel crucible. The embrittled depth was measured as 70 μm with a microscope with an optical micrometer. AES spectra from spalled regions indicated a Be content of over 60 at% and a Ni content of near 25 at%. There were no indications of Li or F. Spectra from surfaces that had not spalled showed similar Be and Ni contents, sometimes minor F indications, but little or no indications of Li. This shows that there was no or little salt adhering onto the crucible. But more importantly, the high Be contents identifies where the Be from the specimen had relocated. A mass balance indicated that the Be in the 70 µm embrittled zone can account for Be lost from the specimen. Diffusion to such depth implies a time dependence mechanism occurring over the long exposure and not merely segregation during cool down and solidification.

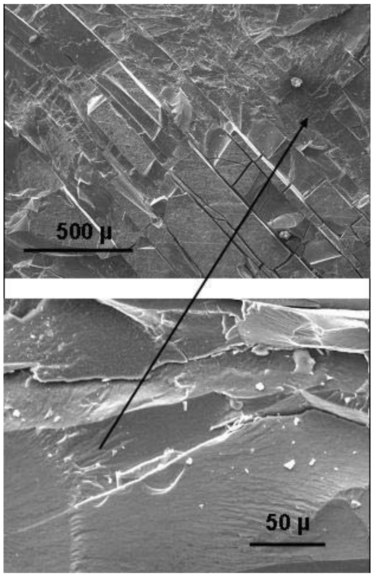

Fig.6. Inner surface of Be6 Ni crucible showing zone embrittled by Be.

Conclusions

The small-scale crucible tests have confirmed that Be loss is accentuated by a galvanic coupling with nickel. The Be is largely transferred to the nickel crucible and diffuses into the Ni container at 803K. Only a small fraction of the Be lost from the specimen remains in the salt. The Be that presides in the salt segregates to outer locations near the crucible interface. It is possible that some of this segregation could occur during cool down. These findings indicate that the small crucible tests have limitations toward measuring Be solubility limits in flibe. However, the values obtained from outer edge salt of 0.1 to 0.4 mol% likely represent a conservatively high approximation of the solubility limit. More appropriate measurements can be obtained from hot sampling. Corrosion from galvanic coupling is dependent upon geometry such as anodic and cathodic surface areas. Projecting behavior from the small crucibles to the larger pot tests with HF purging would be precarious. The extent of attack of the Be specimens, inclusion of Be grains into the salt, and diffusion of Be into the crucible are long term mechanisms in the small-scale tests. We would expect them to be quite limited during the relatively short, less than one hour, Be exposures in the redox tests. It is important to note that the calculated Be loss during the one-hour redox test represent a 0.003 mol% uptake into the salt. This is near the detection limit of the H_2SO_4 dissolution method. We believe this method can be effective in detecting dissolved Be with longer Be dunk times. The redox setup has been equipped to allow hot sampling during runs. We will use this sampling process to evaluate Be uptake in the salt for longer exposures and for measuring impurities during future corrosion tests.

ACKNOWLEDGEMENTS

This work is supported by the U.S. Department of Energy, Office of Energy Research, under DOE Idaho Operations Office Contract DE AC07-05ID14517. The support of Stan Schuetz, Bob Pawelko, and Tammy Trowbridge is acknowledged and greatly appreciated.

REFERENCES

[1] M. Simpson, et al., ICFRM-12 To be presented. Dec. 4-9, 2005.

[2] W.R. Grimes, Molten-Salt Reactor Chemistry, Nuclear Applications & Technology, 8 (1970) 137-155.

[3] M. Hara, Y. Hatano, M.F. Simpson, G.R. Smolik, J.P. Sharpe, Y. Oya, K. Okuno, M. Nishikawa, T. Terai, S. Tanaka, R.A. Andrel, D.A. Petti and D.-K. Sze, Interactions Between Molten Flibe and Metallic Be, Paper pesented at 7th International Symposium on Fusion Nuclear Technology, Tokyo, Japan, May 22-27, 2005.