INL/CON-05-00920
PREPRINT

Beryllium Technology Research in the United States

7th IEA International Workshop on Beryllium Technology

Glen R. Longhurst
Robert A. Anderl
M. Kay Adler-Flitton
Gretchen E. Matthern
Troy J. Tranter
Kendall J. Hollis

February 2005

The INL is a
U.S. Department of Energy
National Laboratory
operated by
Battelle Energy Alliance

BERYLLIUM TECHNOLOGY RESEARCH IN THE UNITED STATES

GLEN R. LONGHURST*, ROBERT. A. ANDERL, M. KAY ADLER-FLITTON, GRETCHEN E. MATTHERN, TROY J. TRANTER, *Idaho National Laboratory, P.O. Box 1625, Idaho Falls, Idaho, 83415 USA*

KENDALL J. HOLLIS *Los Alamos National Laboratory, P.O. Box 1663, Los Alamos, New Mexico 87545 USA*

ABSTRACT

While most active research involving beryllium in the United States remains tied strongly to biological effects, there are several areas of technology development in the last two years that should be mentioned. (1) Beryllium disposed of in soil vaults at the Idaho National Laboratory (INL) Radioactive Waste Management Complex (RWMC) has been encapsulated in-situ by high-temperature and pressure injection of a proprietary wax based material to inhibit corrosion. (2) A research program to develop a process for removing heavy metals and cobalt from irradiated beryllium using solvent extraction techniques has been initiated to remove components that prevent the beryllium from being disposed of as ordinary radioactive waste. (3) The JUPITER-II program at the INL Safety and Tritium Applied Research (STAR) facility has addressed the REDOX reaction of beryllium in molten Flibe (a mixture of LiF and BeF_2) to control tritium, particularly in the form of HF, bred in the Flibe by reactions involving both beryllium and lithium. (4) Work has been performed at Los Alamos National Laboratory to produce beryllium high heat flux components by plasma spray deposition on macro-roughened substrates. Finally, (5) corrosion studies on buried beryllium samples at the RWMC have shown that the physical form of some of the corroded beryllium is very filamentary and asbestos-like.

KEYWORDS: *beryllium, disposition, transmutations, transuranic, flibe, plasma spray, disease*

I. INTRODUCTION

By far, the greatest expenditures for research in the United States involving beryllium has been in the realm of biological effects. Weitzman estimated in 2003 that research opportunities for beryllium health and safety research were approximately $14.6 million.[1] In contrast, work performed in development of beryllium technology combined was much less. Most of the technology development activity was connected with management of irradiated beryllium wastes.

*E-mail: Glen.Longhurst@inl.gov

It was discovered in 1999 that irradiated beryllium disposed of at the RWMC was corroding with attendant release of tritium and ^{14}C.[2] In 2001, it was found that beryllium irradiated in the Advanced Test Reactor (ATR), and by inference in most fission reactors, required classification as Transuranic Waste. Under U.S. environmental law, such material could not be disposed of in existing repositories for radioactive waste, and an exploration of processing techniques has been initiated.

Fusion reactors are planned that make use of beryllium in two ways. One use is as a low-atomic-number plasma-facing material with excellent oxygen gettering capabilities. The other potential use is as Flibe coolant and tritium source in breeding blanket designs. Production of such beryllium plasma-facing components and control of tritium in the Flibe are motivations for some of the work reported here.

II. ENCAPSULATION OF BURIED Be WASTE

Beryllium waste in the RWMC Subsurface Disposal Area contains tritium from neutron activation of beryllium. This waste is buried at depths of 6 m or less. As the beryllium corrodes, tritium is released into the surrounding soil as gas or water vapor. A beryllium encapsulation project has been conducted at the INL to prevent further corrosion of the beryllium by keeping water away from it.[3] Known and suspected beryllium disposal areas were surveyed for tritium at soil depths of 15.2 cm and 61 cm below ground surface. Tritium anomalies were used to identify sites needing treatment.

In situ high-pressure jet grouting was used to isolate the beryllium blocks without removing them from their burial location. In addition to preventing water from reaching the blocks, this technique reduces migration of contaminants (primarily C-14) from the beryllium blocks and reduces subsidence potential to prevent pooling of water. It will be repairable if isolation is breached, and it will allow future retrieval if required.

Several potential grouts were tested and compared based on the required criteria of effectiveness and ease of application. The conclusion was that the paraffin-based grout WAXFIX was superior to other grouts tested.[4] WAXFIX is a proprietary grout available from Carter

Technologies Co. in Houston, Texas. It has a melting point of about 51.7°C and a specific density of about 0.8.

A private company was awarded the contract to provide the required equipment and services. The major pieces of equipment used in jet grouting beryllium blocks included:

- Grout containment units (GCUs), which contained the potentially contaminated returns from the jet grouting process
- Drill rig, which performed the drilling and jet grouting operations
- High-pressure pump, which supplied the grout to the drill rig at high pressure
- Grout truck, which transported hot WAXFIX from the storage site to the drilling site.

Holes were drilled through the GCUs to a depth below the bottom of the beryllium in an array configured to get full penetration of the region containing the buried beryllium. The pump supplied grout at 500 bar and more than 90°C. Prior testing had shown the extent of penetration of the hot grout in the soil. After injection for a predetermined time through the drill, the drill rig was raised by a few cm, and the process was repeated until it got near the surface.

Among the problems encountered was the quantity of grout and soil returned to the surface during grouting operations. A number of solutions were considered, but the problem was dealt with by cleaning out the GCUs with a backhoe. Other problems, such as vibrating the nozzles out of the monitor while drilling and breaking of drill rods, also were encountered and solved. The project took 11 months to complete. In all, 512 holes were drilled and grouted.

III. REMOVAL OF HEAVY METALS AND COBALT

During routine activation calculations on beryllium used as neutron reflectors in fission reactors, it was discovered that uranium impurity concentrations of only a few mg/kg could result in the waste being classified as transuranic (TRU), having more than 100 nCi/g of radioactive elements with atomic numbers greater than 92 and half-lives greater than 20 years. Such waste presently has no pathway for disposal in the U.S. Analyses and measurements on beryllium from the Advanced Test Reactor at the INL confirmed concentrations of heavy metals that were about five times the threshold for TRU classification.[5] Additionally, iron and cobalt impurities activate to ^{60}Co, whose gamma radiation fields make it necessary to remotely handle irradiated beryllium.

For example, as of September 2001, blocks from the third ATR core, irradiated from August 1977 to February 1986, were determined to have 461 nCi/g of transuranics (mostly ^{241}Pu and ^{244}Cm), 12.6 μCi/g of ^{137}Cs, 3.3 μCi/g of ^{154}Eu, and 3.7 μCi/g of ^{90}Sr, all due to an initial uranium impurity of 30mg/kg. They also held 31.3 mCi/g of ^{60}Co and 235 mCi/g of ^{3}H from activation of the beryllium itself.[6]

A small research program has been initiated to evaluate techniques for removing these contaminants from irradiated beryllium such that the beryllium can be disposed of as ordinary radioactive waste. Recycling is not a current objective. The separated radioactive metals may then be disposed of separately in a high-level waste repository or burned away in a fission reactor.

The research performed in the first year has shown that beryllium can be successfully dissolved in nitric acid and that isotopes of Cs, Sr, Pu, and Am can be successfully removed using a combination of two solvent extraction approaches.[7] The results indicate that greater than 99.9% removal can be achieved for each isotope with only three contact stages. Increasing the number of extraction stages should provide even greater removal efficiencies.

Work will continue in the next year to develop a suitable technique for ^{60}Co removal. Column supported dimethyl glyoxime will be investigated for this purpose as well as several ion exchange approaches. Work will also continue with the target isotopes mentioned above to investigate the possibility of using a combination of extraction chromatography and ion exchange to provide an alternative approach to solvent extraction for removing these isotopes.

IV. TRITIUM IN FLIBE

Much of the beryllium in some fusion reactor designs will be in molten salt. Flibe, a mixture of LiF and BeF_2, is being considered as a coolant for breeding blankets with the added capability of breeding some tritium. The JUPITER-II program is supporting research on Flibe at the Safety and Tritium Applied Research (STAR) facility at the Idaho National Laboratory. Safety and performance issues arising from the corrosive properties of TF, produced in the Flibe by neutron transmutation and chemical composition, are being investigated.

A REDOX process has been developed for controlling pH in the Flibe using sacrificial beryllium to react with the TF. Recent experiments have examined the dissolution rate of beryllium in the molten Flibe as a function of various flow and chemical parameters. A further goal is to understand the mechanisms by which beryllium is transported in the molten salt after dissolution and how and where it interacts with the TF.

REDOX experiments were conducted in which He, H_2, and HF were bubbled through molten Flibe. Mass spectroscopy and titration at the gas outlet measured the amount of HF in the gas stream. Experiment results showed very clearly that when a beryllium rod was inserted into the molten Flibe, the HF essentially disappeared from the gas stream. This illustrates the effectiveness of sacrificial beryllium as a corrosion suppressant in Flibe systems.

Also among the findings of these experiments is that dissolution of the beryllium is tied to galvanic coupling. Fig. 1 shows two beryllium rods immersed in Flibe at 530°C for 150 hours in nickel crucibles. The top rod was electrically coupled to the crucible while the bottom one was electrically insulated. Only a 3-mm metallic core remained in the top rod from an initial diameter of 5.1 mm. Dark material on the end of the rods is thought to be solidified Flibe with contaminants.

FIG. 1. Beryllium rods immersed in molten Flibe at 530°C for 150 hours demonstrated the effect of galvanic coupling in accelerating beryllium dissolution. The top rod was electrically coupled to the nickel crucible while the bottom rod was insulated from it.

Another finding from analysis of the crucibles and of grains of solidified Flibe following the experiment was that the dissolved beryllium clearly migrated to the wall of the nickel vessel and even diffused into them.

More information on this work will be forthcoming.[8]

V. PLASMA-SPRAYED COMPONENTS

The energy from the highly energetic particles in a magnetically confined fusion reactor plasma is deposited primarily in the divertor and blanket regions of the reactor. These regions serve to protect the remainder of the reactor from high heat loads. The area of the blanket facing the high temperature plasma is called the first wall (FW). For the International Thermonuclear Experimental Reactor (ITER), the FW heat flux absorbed is expected to be 0.25 MW/m^2 on average with a maximum of 0.5 MW/m^2. The pulse length for heating is approximately 400 seconds with a pulse repetition period of as short as 1800 seconds. Over the lifetime of ITER the number of pulses could exceed 30,000. The material on the outer surface of the FW (facing the plasma) is beryllium metal. The Be thickness on the FW is 10 mm and the maximum allowable surface temperature during operation is 700°C. The total surface area of the Be FW is 680 m^2. The Be is attached to a water-cooled copper alloy heat sink that is bonded to a water-cooled stainless steel structure.

Plasma spraying is being considered for the initial fabrication and the repair of the FW. Plasma spraying allows the production of FW components from Be powder in one step versus a bonded tile approach which requires hot pressing the Be powder, machining the tiles, and bonding the tiles to the heat sink to produce the FW components.

The primary technical challenge to plasma spraying Be on a copper alloy heat sink is the control of stresses that result from the spraying process and stresses that result from the thermal and mechanical loads which impinge on the component during use in the fusion reactor. Careful consideration of the coefficient of thermal expansion (CTE) mismatch between the coating and substrate and thermal stresses which arise during fabrication and in service is necessary to produce a coating that will survive both fabrication and deployed service. Therefore, strain tolerance and controlled stress relief are properties of critical importance for ITER FW applications. Experiments being conducted at the Los Alamos National Laboratory are seeking to develop such technology.

The experiments incorporated macro-roughening of the substrate as a means of increasing performance in cyclic high heat flux conditions. The substrate material used was Cu-0.65Cr-0.1Zr alloy (CuCrZr), 58 mm long by 22 mm wide by 19 mm high. The center of the substrate contained a 10 mm diameter coolant passage with coolant tubes extending from each end of the sample. A total of six substrates were macro-roughened and coated with Be. Three samples were coated to a Be thickness of 10 mm and the other three were coated to a Be thickness of 5 mm.

Four of the substrates were machined with cubic projections. Two of those had cube lengths and separations of 3 mm while the other two had lengths and separations of 1.5 mm. The larger cubes were coated with 10 mm of Be and the shorter cubes were coated with 5 mm of Be. In addition, a dovetail projection was also used. The dovetail height was 2.3 mm with a maximum width of 4.7 mm and a sidewall angle of 75°. Coatings of 5 and 10 mm were deposited on the same dovetail patterns. Gas atomized spherical Be powder (product O-30 from Brush Wellman, Inc., Cleveland, OH) was used. This powder had a rather broad size range, from <5 to >74 μm, and oxygen (0.64 wt%) and carbon (0.086 wt%) were the principal impurities. Fig. 2 shows one of the coated specimens.

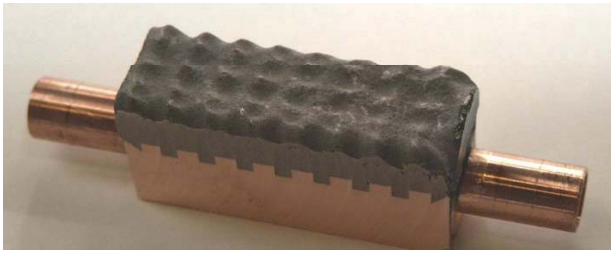

FIG. 2. Sample with 3-mm cubic projections machined into the Cu alloy substrate and plasma sprayed with 10 mm of beryllium.

The four samples with cubic projections were tested in the Jülich Divertor Test Equipment in Hot Cells

(JUDITH) electron beam facility at Forschungszentrum, Jülich, Germany. The 5 mm thick samples were heated for 10 seconds then cooled for 10 seconds while the 10 mm thick samples were heated for 15 seconds and cooled for 15 seconds per cycle. The samples were cooled with water at 20°C flowing 1.0 l/s. The absorbed heat flux and number of cycles were chosen to be similar to that present in ITER. The absorbed heat flux was increased until the sample under test showed a surface temperature of 800°C.

The two samples with dovetail projections were tested at the Plasma Materials Test Facility at Sandia National Laboratories in Albuquerque, New Mexico, using the 30-kW Electron Beam Test System (EBTS).[9] The samples were heated for 10 seconds and cooled for 15 seconds per cycle. The samples were cooled with water at 8-20°C flowing 0.79 l/s. Like the testing at JUDITH, the absorbed heat flux and number of cycles were chosen to be similar to that present in ITER. The absorbed heat flux was increased until the sample under test showed a surface temperature of 800°C or sample damage was observed.

Results showed that cubic and dovetail substrate projections prevent edge lifting of 5 mm and 10 mm thick Be coatings during fabrication by low-pressure plasma spray and testing under ITER first wall relevant conditions. In addition, the coatings have low porosity (< 2%) away from the macro-roughening features, and appear to avoid beryllium/copper intermetallic formation at the coating/substrate interface.

All samples in this study exceeded the ITER required average heat flux of 0.25 MW/m^2 and maximum heat flux of 0.5 MW/m^2 before damage was detected. Damage in the 10 mm thick Be coating samples occurred at 4.6, 8, and 10 times the average expected heat flux of 0.25 MW/m^2. For the 5 mm thick Be coating samples, damage occurred at 10, 12, and 13.6 times the average expected heat flux. The samples had similar thermal conductivity values based on a comparison of surface temperatures at a given absorbed heat flux for the 5 mm thick coating samples. Despite the similar thermal conductivity, the absorbed heat flux where damage occurred was higher for the cubic macro-roughened samples than for the dovetail macro-roughened samples. Further information on this work may be found in Ref. [10].

VI. UNUSUAL BERYLLIUM FORM

Recent work at the INL on beryllium corrosion[11] has shown a needle-like structure of beryllium on corrosion coupons. The INL studies were conducted to evaluate in-situ corrosion of various materials disposed of in the Subsurface Disposal Area (SDA) of the RWMC. Samples of several materials, including beryllium, were buried in the soil at the RWMC in a manner and under soil conditions similar to those of radioactive wastes buried there. Samples were removed after 1, 3 and 6 years and examined for corrosion. Electron microscope images of the corroded beryllium surface were surprising. Fig. 3 illustrates.

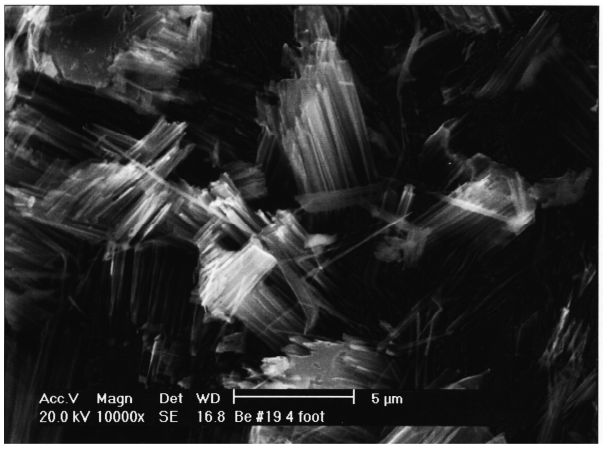

FIG 2. High magnification electron microscope image of beryllium corroded in the ground including some that appear to be free fibers.

Notice the fibrous nature of the corroded beryllium surface. Edges of the grains show needle-like structures in various stages of formation, and some appear even detached. This is a far different formation than the hexagonal close-pack crystals usually seen in material that has been pressed or is ready for compaction. These needle-like formations may not be unique to beryllium that has been underground. However, these structures in beryllium have not been reported before. The observation of such fibers in corroded beryllium suggests it would be useful to search for similar fibers in various workplace environments.

VII. CONCLUSION

Progress is being made in the U.S. in a variety of different areas of beryllium technology relevant to nuclear applications. Among the most prominent are in the areas of disposition of irradiated beryllium, preparation of plasma-sprayed beryllium coatings for plasma-facing applications, and interactions of beryllium with molten salts. Recent discoveries on the physical form of corroded beryllium suggest further research may be warranted to investigate the extent to which they may be present in the workplace.

REFERENCES

1. D. Weitzman, November 2007, “Beryllium Research Agenda,” 2003 EFCOG/DOE Chemical Management and Beryllium Workshop, November 4-6, 2003, DOE Forrestal Headquarters, Washington D.C., Internet, http://www.eh.doe.gov/chem_safety/ws2003/WEITZMAN.pdf, accessed September 19, 2005.
2. P. D. Ritter and D. L. McElroy, March 1999, *Progress Report: Tritium and Carbon-14 Sampling at the Radioactive Waste Management Complex*, INEEL/EXT-

98-00669, Idaho National engineering and Environmental Laboratory, Idaho Falls, Idaho.

[3]. S. L. Lopez et al., January 2005, *Summary Report for the OU 7-13/14 Early Actions Beryllium Encapsulation Project*, ICP/EXT-04-00646, Rev. 1, Project No. 24059, Idaho Completion Project, Idaho Falls, Idaho

[4]. Hanson, D. J.et al., 2004, *Evaluation of the Durability of WAXFIX for Subsurface Applications*, ICP/EXT-04-00300, Idaho Completion Project, Idaho Falls, Idaho.

5. G. R. Longhurst, "Irradiated Beryllium Disposal Issues, Background, Measurements, and Concerns," in G. R. Longhurst et al., July 2002, *Irradiated Beryllium Disposal Workshop, Idaho Falls, Idaho, May 29 & 30, 2002*, INEEL/EXT-02-00785, Idaho National Engineering and Environmental Laboratory, Idaho Falls, Idaho.
6. C. K. Mullen et al., March 2003, *Beryllium Waste Transuranic Inventory in the Subsurface Disposal Area, Operable Unit 7-13/14*, INEEL/EXT-01-01678, Rev. 2, Idaho National Engineering and Environmental Laboratory, Idaho Falls, Idaho.
7. T. Tranter et al., "Process Development for Treating Irradiated Beryllium for Disposal," this workshop.
8. G. Smolik et al., 2005, "Beryllium Interactions with Molten Flibe," 12th International Conference on Fusion Reactor Materials, December 4 – 9, 2005, Santa Barbara, California.
9. D.L. Youchison, J.M. McDonald, L.S. Wold, 1994, High Heat Flux Testing Capabilities at Sandia National Laboratories, New Mexico, HTD-vol. 301, A.M. Khounsary, Ed., *Heat Transfer in High Heat Flux Systems*, ASME Book No. G00956.
10. K. J. Hollis et al., "Plasma Sprayed Beryllium on Macro-Roughened Substrates for High Heat Flux Applications," to be published in *Journal of Thermal Spray Technology.*

[11]. M. K. Adler Flitton et al., September 30, 2004, *Long Term Corrosion/Degradation Test Six Year Results,*" INEEL/EXT-04-02335, Idaho National Engineering and Environmental Laboratory, Idaho Falls, Idaho.