GA–A25729

INVESTIGATION OF DEUTERIUM PERMEABILITY OF SPUTTERED BERYLLIUM AND GRADED COPPER-DOPED BERYLLIUM SHELLS

by

A. NIKROO, H.W. XU, K.A. MORENO, K.P. YOUNGBLOOD, J. COOLEY,
C.S. ALFORD, S.A. LETTS, and R.C. COOK

JANUARY 2007

GENERAL ATOMICS

DISCLAIMER

GA–A25729

INVESTIGATION OF DEUTERIUM PERMEABILITY OF SPUTTERED BERYLLIUM AND GRADED COPPER-DOPED BERYLLIUM SHELLS

by
A. NIKROO, H.W. XU, K.A. MORENO, K.P. YOUNGBLOOD, J. COOLEY,*
C.S. ALFORD,† S.A. LETTS,† and R.C. COOK†

This is a preprint of a paper presented at the 17th Target Fabrication Specialist Meeting, San Diego, California on October 1-5, 2006 and to be published in *Fusion Science and Technology.*

*Los Alamos National Laboratory, Los Alamos, New Mexico.
†Lawrence Livermore National Laboratory, Livermore, California.

Work supported by
the U.S. Department of Energy
under DE-AC52-06NA27279 and W-7405-ENG-48

GENERAL ATOMICS PROJECT 30272
JANUARY 2007

GENERAL ATOMICS

INVESTIGATION OF DEUTERIUM PERMEABILITY OF SPUTTERED BERYLLIUM AND GRADED COPPER-DOPED BERYLLIUM SHELLS

A. Nikroo, H.W. Xu, K.A. Moreno, K.P. Youngblood, J. Cooley,*
C.S. Alford,† S.A. Letts,† and R.C. Cook†

General Atomics, P.O. Box 85608, San Diego, CA 92186
*Los Alamos National Laboratory, Los Alamos, NM 87544
†Lawrence Livermore National Laboratory, Livermore, CA 94550
nikroo@fusion.gat.com

Graded copper-doped Be shells have been fabricated by sputter coating on spherical mandrels. While such coatings have consistent microstructure and acceptable void content and size, we have found that they suffer from sufficient interconnected porosity leading to relatively rapid gas leakage. In this paper, we present an extensive study of D_2 leakage out of Be shells made by sputter coating. The leakage appears to follow molecular flow dynamics as determined by examining the temperature dependence of the flow. Furthermore, the time dependence of the leakage suggests that the flow channels are nanometerish in diameter, propagating through the thickness of the coating, possibly brought about by residual stress in the coatings. We have investigated the D_2 leakage time constant as a function of a large number of coating parameters, including the effect of introducing boron-doped layers. Addition of thin 0.25 μm amorphous boron-doped layers near the inside surface has been most effective in producing shells with long time constants (greater than 7 days to immeasurable) with yield of greater than 50%. There is still substantial scatter in the data, even within a given coating batch, suggesting a possible stochastic cracking process driven by residual stress in the coating.

I. INTRODUCTION

A graded copper-doped beryllium (Be:Cu) capsule is required for the current ignition point design[1] for experiments to take place at the National Ignition Facility[2] (NIF) starting in 2009. Such capsules are produced by sputter coating beryllium (Be) and copper-doped beryllium on appropriate spherical mandrels, typically CH in composition,[3] while they are agitated to obtain uniform coatings. In addition, the point design requires that the capsules meet certain dimensional, density, x-ray opacity and roughness specifications. The coating process has been described previously in several articles, which represent its evolution.[4-6] The latest developments in the coating process and our progress in meeting the demanding design specifications are detailed in the paper by H. Xu, *et al.*[7] in this issue.

In this paper, we focus on the unexpected leakage of deuterium (D_2), with half-lives as short as a few minutes, from our sputter deposited Be shells. Although sputter coatings, in particular when deposited on non-flat substrates such as a shell, have always suffered from voids, totaling about 5% or more, previous transmission electron analysis (TEM) did not suggest connectivity of these voids. The evidence gathered in this study indicates molecular flow as being responsible for the escape of gas from the shells, pointing to connected nano-channels in the coatings. The origin of such nano-channels is traced to the quality of the coating itself, which as mentioned above is compromised by the non-flat geometry of the substrate and the resulting induced self-shadowing. The ubiquitous columnar structure of the coatings is conjectured to promote nano-cracking, with the columns separating from each other under residual tensile stresses, and aided by the aforementioned intercolumnar voids.

Deuterium gas retention of ignition shells is of utmost importance for cryogenic loading of the DT fuel and fielding of the capsule. The minimum required fill half-life depends on two factors, both of which yield the requirement of a few hours of D_2 half-life at room temperature. First is the allowable leakage in the time it takes to load the fuel into the shell at room temperature and to transport and solidify it in the cryogenic system, which is a few hours. The second is the rate of leakage at cryogenic temperature by sublimation and subsequent leakage through the channels during the up to 30 h layering time. To allow some orders of magnitude of safety margin we have picked as our goal a one-week room temperature half-life for our capsules.

To increase Be:Cu shell gas retention, a number of variations in the coating process, expected to yield a coating with lower void content, were examined as well as the presence or lack of copper (Cu) doping in the coatings. However, addition of 10-15 atomic % boron (B) to the Be in thin layers within the first micron of coating decreased the gas leakage by orders of magnitude, from minutes to weeks with a yield of about 50%. At this concentration it is known that a glassy alloy forms.[8,9] The formation of multilayers by sputtering is well known and has been used before for various purposes, but typically the layers are very thin (nm). Multilayers have been used to break up the microstructure and provide oxidation resistance,[10] but the use of relatively thick (100’s nm) glassy layers to form an effective leakage barrier is new. In what follows we will detail our experimental methods, including our techniques for measuring the gas retention half-lives. We will then discuss first our largely unsuccessful attempts to reduce the leakage by modifying our processes, before reporting our success with thin B-doped (Be:B) layers within the first micron of coating.

II. EXPERIMENTAL

The coating process in its current form is detailed elsewhere.[5-7] The results presented here are those from coatings in four different coaters at two different locations, at General Atomics in San Diego and the Lawrence Livermore National Laboratory in Livermore. The variations in the basic coating process were performed in at least two different coaters to eliminate possible coater-to-coater differences. The variations involved inclusion of Be:B layers as mentioned above, as well as others, which we will classify as those involving non Be:B layers. These latter variations are described here. The first was the introduction of an oxide layer by interrupting the run and allowing the Be surface to oxidize in-situ in the chamber, or explicitly by pulsing oxygen into the coater at various points during the coating. This was designed to interrupt columnar growth and thus possibly the columnar structure, and hence interrupt the interconnected channels. The second approach was to negatively bias the pan to induce argon ion bombardment of the Be coating to increase its density and reduce voids. In addition, the biasing was expected to promote more compressive residual stress, thus reducing tensile separation of the columns. This biasing was achieved by isolating the normally grounded pan holding the shells using a ceramic spacer. The pan was biased to -80 V for these experiments, which had previously been reportedly to produce good results as far as surface finish was concerned.[4] The coating pressure was also adjusted between 2 mTorr, the lowest pressure at which a plasma could be ignited, and 12 mTorr. Such changes in pressure were expected to change the stress in the coating, with the coatings at lower pressure producing a denser structure with a more residual compressive coating. Be:B layers mentioned above were produced by co-sputtering Be and B from different sputter sources. The B concentration in Be was based on the measured coating rates of two materials. In our experiments, B concentrations from 8% to 21% and layer thicknesses of 0.25 μm to 6 μm were produced and tested. The location of the doped layers was also varied from within the first μm of the shell to as much as 60 μm from the inner shell surface.

The ignition design requires 170 μm thick coatings, which at the nominal coating rate of 0.4 μm/h and the required sputter target changes every week of continuous running, take about 3 weeks to complete. To expedite data collection, we initially deposited coatings and tested shells at thicknesses of 50-60 μm for each variation. We then deposited thicker coatings for the most promising approach, which was with the inner 1 μm containing Be:B layers as we shall see below.

Beyond examining the effects of the coating itself, we examined possible effects of other steps in the process of making a free standing Be:Cu shell, as shown in Fig. 1, namely laser drilling,[11] which could possibly deposit sufficient energy in the shell to cause heating and rapid cooling induced cracking, and the mandrel removal process[12] which can further induce cracking due to BeO formation between columns or grains due to oxidation when the shell is heat treated.[13] To test the effect of laser drilling, we coated CH mandrels that already had laser drilled 50 μm holes in their walls. After 50 μm of Be coating, these holes were still open and the mandrel could be removed without drilling. Typically the mandrel is removed thermally by heating the capsule to 400°-550°C in air.[12] To examine lower temperatures and oxygen free mandrel removal we deposited Be coatings on poly(α-methylstyrene) (PAMS) mandrels,[14] which could be removed in nitrogen at 300°C or washed out using a solvent at room temperature.

As mentioned above, after Be coating, the shells were laser drilled and the inner plastic mandrels were burned out in air at 400°-550°C through the 7-15 μm hole.[12] To test D_2 retention, the Be shells were then loaded in a pressurized cell filled with D_2 and then sealed under pressure with UV cure epoxy. The D_2 gas contained 0.4 atom% argon (Ar) for reasons explained below. The sealing chamber could be filled to as much as 35 atm,

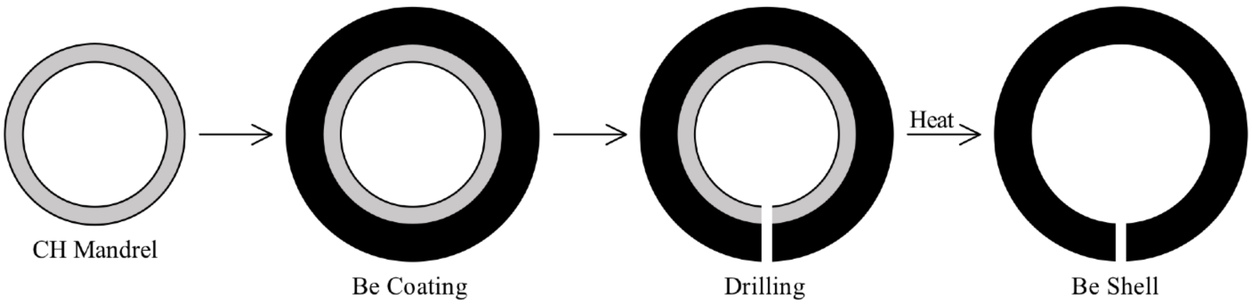

Figure 1. Freestanding beryllium shells are produced after removing the mandrel through a laser drilled hole in the Be coating.

although most tests were done at 20 atm. Shells were also tested at 5-10 atm to rule out any possible effect (stretching) of the internal burst pressure on the shells. The sealed Be shell was then introduced into a mass spectrometer (MS) within minutes after sealing. The mass spectrometer has been used previously for measurement of half-lives of minutes to weeks.[15] If the half-life is greater than about 70 days the MS signal is so low that it cannot be distinguished from the background noise. However, a signal in the noise could also mean that the shell was a very quick leaker and all the D_2 had escaped before it could be measured in the MS. The trace Ar in the D_2 fill was then used to distinguish between these two scenarios. If the shell was gas retentive then the Ar content could be detected by x-ray fluorescence (XRF). Half-lives were also measured at 77 K in the MS system by immersing the chamber holding the shell in liquid nitrogen.

The measured D_2 half-life was further confirmed on a large subset of the shells examined by crushing the sealed shells in a fixed volume. The gas pressure in the shell after the crush test could be extracted from the pressure rise of a fixed volume. In this way, the D_2 half-life could be deduced by comparing the remaining pressure in the shells after a known period of time to the pressure the shells were filled to in the sealing chamber. The error in this measurement was less than 5%. The deviation between the two techniques (and hence basically the error in the MS measurement) for half-lives of minutes to several hours was less than 20%. The crush test in general yielded longer half-lives than those measured by MS by as much as a factor of two for shells with half-lives in the 1 day range. This might have been due to entrapped gas in the shell wall escaping in the mass spec more quickly than the gas in the shell, yielding a lower half-life. In any case, the MS results then have error bars of as much as a factor of two with an absolute value of about 1 day, and represent an underestimation of the half-lives. For comparative purposes, where several orders of magnitude increase in half-life needed to be achieved and measured, such a relatively large error was not an issue.

A number of shells were examined by submersion in glycerol which allowed observation of D_2 bubbles formed at the shell surface. An example is shown in Fig. 2 of a shell with about a 2 hour half-life, indicating numerous leakage paths for these poor performing shells. Such examination provided a valuable visual clue to the magnitude of the leakage paths, which together with the half-life are used to estimate the leakage channel size.

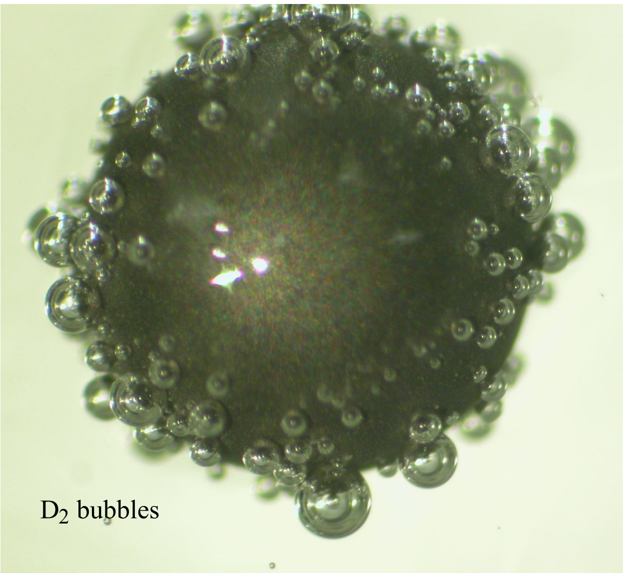

Figure 2. Photo of a bubble test of a Be shell with a 2 h half-life. The shell was immersed in glycerol shortly after being filled with 20 atm of D_2. The bubbles provide a visual guide of the leakage path locations and numbers.

III. RESULTS AND DISCUSSIONS

We first established that the major source of gas leakage was not the laser drilling or mandrel removal. Shells never having experienced drilling by coating on drilled mandrels still leaked as fast as those with laser drilled holes. These half-lives ranged from minutes to hours, which were typical for the baseline coatings.[5-7] We found that higher or lower mandrel removal temperatures also did not significantly improve the gas retention compared to the nominal 400°C. In particular, washing the mandrel out through the hole at room temperature, where no thermal stresses are exerted on the shell, did not have a significant effect on the leakage. The Cu-doped or undoped Be shells performed equally poorly ruling out any beneficial or detrimental effect due to Cu doping.

Therefore, changes to the coating process were pursued. However various variations (bias, pressure, …) did not produce any statistically significant improvement, except for incorporation of Be:B layers. The use of statistics is required here given the spread of values observed within a batch, from typically a few minutes to several hours to several days. The results are summarized in Fig. 3. The data is divided between variations not involving Be:B layers, such as low and high coating pressures, -80 V biasing, growth interruption during coatings, and pulsing oxygen to the chamber during coating; and those with Be:B layers. None of the conditions used with Be shells only seemed to change the columnar grain structure and the short D_2 retention half-life. The Be:B layers also did not improve the half-lives significantly if the layers were not in the first micron of the coating. In contrast, when two 0.25 μm, 10-15 at% Be:B layers were incorporated into the first μm of the Be coating, many shells had D_2 half-lives that were above 7 days. The gas retention improvement is statistically significant at the 99% confidence level. It is important to realize that the data shown in Fig. 3 is representative of over one hundred shells tested in each category. Figure 4 shows the results of 6 different controlled runs using two 0.25 μm Be:B layers in the inner one μm of shell. The yield of shells having greater than a 7-day half-life is 58% for these controlled runs.

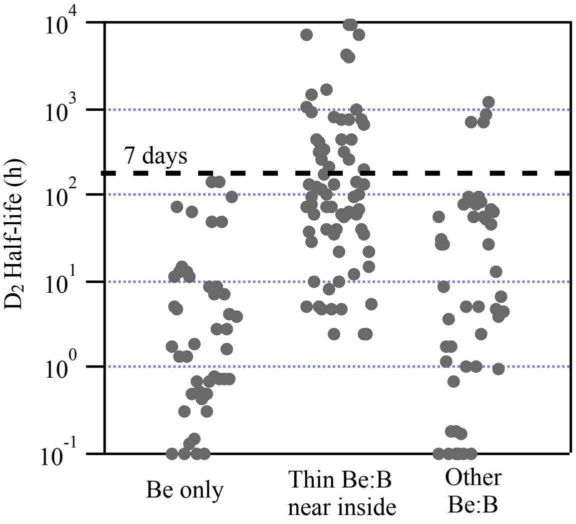

Figure 3. This figure compares the D_2 half-lives of shells without Be:B layers, with two 0.25 μm Be:B layers within the inner 1 μm of the shell, and other Be:B layer geometries. Notice the log scale. Despite the scatter in the data, it is clear that shells with Be:B layers within the inner 1 μm had much longer half-lives.

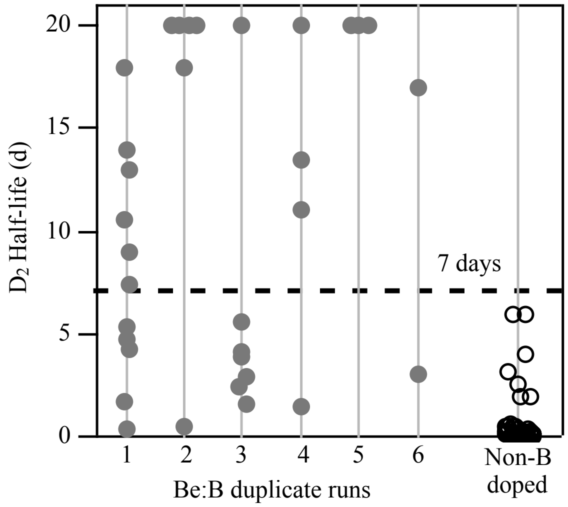

Figure 4. This figure contains a subset of the data shown in Fig. 3. Shown are the results of 6 controlled runs with two 0.25 μm 10-15 at% Be:B layers in the inner μm of the shells. For the purposes of this plot measured half-lives in excess of 20 days are reported at the 20 days. The yield of shells with D_2 half-lives of greater than 7 days is 58%.

We believe reason for the observed improvements can be traced to the leakage mechanism. Beryllium is virtually impermeable to D_2, especially at room temperature. Thus the leakage must be through a flow mechanism involving channels in the coating. The columnar structure of the coatings can lead to formation of possible connected channels through which gas can escape. Since the number of such channels appears to in the hundreds to a few thousand based on the glycerol tests, the effective diameter of such channels needs to be in the nanometer regime, and this molecular flow (as opposed to viscous flow) is the main transport mechanism for the measured D_2 half-lives of minutes to hours. To further confirm the molecular flow assessment, Fig. 5 shows measurements of the half-lives of individual shells at two different temperatures, room temperature and that of liquid nitrogen (77 K). The relative decrease in the half-life is nearly a factor of 2, consistent with the predictions of molecular flow transport scaling as $1/T^{1/2}$. Viscous flow by comparison has virtually no temperature dependence due to reduction of gas viscosity as well as the pressure, both nearly linearly with temperature.

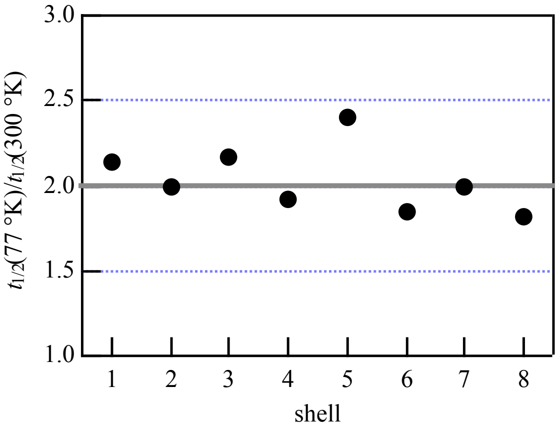

Figure 5. Plotted is the ratio of the measured half life at 77 K to the measured half life at ambient temperature for eight individual shells. The ratio 2 is consistent with molecular flow.

TEM data show that in the columnar grained Be coatings there exist intra and intercolumnar fine striation type voids with dimensions of a few nm wide and a few microns in length.[7] The column boundaries are expected to be weaker than intracolumnar regions and thus more prone to possible nano-cracking. Connectivity of such structure then can be easily envisioned leading to the observed leakage. Interrupting the columnar grain growth using the glassy Be:B layers stops such nano-channels. However, we find that such layers only seem to be effective if placed at the inner part of the shell before the columnar structure has fully taken shape.

A TEM image of the cross section of a shell with two 0.25 µm Be:B layers in the inner 1 µm of the shell is shown in Fig. 6, which shows amorphous Be:B layers which interrupt the columnar grain growth of the Be. However, high resolution TEM images also show that some fine striation line voids penetrate the amorphous Be:B layers. This may explain the scatter in half-life data for Be shells with Be:B layers. Such layers placed further from the inside of the shell were not effective as shown in Fig. 3. A thicker Be:B layer on the inner part of the shell also did not result in shells with improved half-life. However, the major failure mechanism for these layers was catastrophic cracking of the glassy layer. These results point to an optimal thickness (about 0.25 µm) of the amorphous Be:B layers placed near the inside (first µm) of the shells.

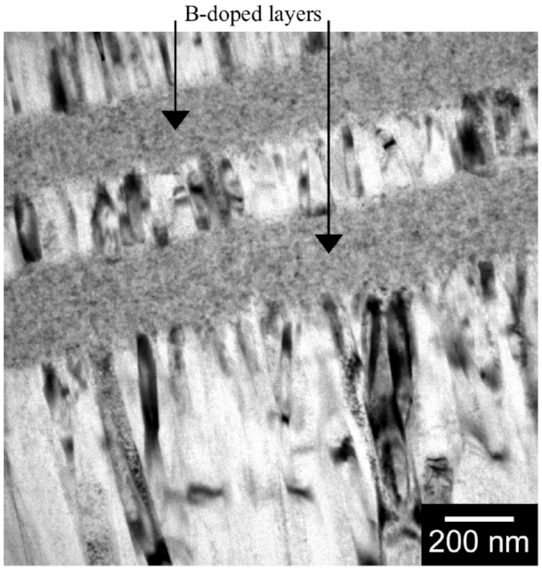

Figure 6. Shown is a TEM image of the glassy Be:B layers in the inner micron of the coating. Selected area diffraction confirmed the amorphous nature of the layers. These layers interrupt the columnar nature of the Be and stop gas leakage dramatically. Small crack-like voids within the amorphous layer lead to finite leakage in some shells.

Finally, full thickness graded Be:Cu shells were produced which contained the 0.25 µm layers in the inner 1 µm. These full thickness shells were made in three coating runs of about 55 µm in thickness. At each stoppage point, a few shells were also tested to confirm the shells gas retention. The half-lives were greater than one day for all shells, with 70% of the full thickness (165 µm) shells having half-lives of greater than the required 7 days.

IV. CONCLUSIONS

Standard sputtered Be and Be:Cu shells leak D_2 at room temperature with half-lives of from minutes to hours as measured by MS and crush testing. Connected nano-channels appear to be responsible for the observed leakage with D_2 being transported by molecular flow. The major reason for the leakage is the quality of the coating itself rather than the post coating steps such as laser drilling and mandrel removal. Addition of two 0.25 µm thick Be:B layers in first 1 µm of coating increased the D_2 half-lives of Be shells to greater than 7 days with yields of $\geq$ 50%. These sputtered Be:B layers had doping at the

10-15 at.% level which resulted in an amorphous structure. To be effective, these glassy layers must be placed on the inner part of the shells before the full development of the usual columnar structure of the sputtered material.

ACKNOWLEDGMENT

This work was performed under the auspices of the U.S. Department of Energy by General Atomics under Contract DE-AC52-06NA27279 and by the University of California Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48. The authors are pleased to acknowledge useful conversations with S. Bajt, J. Taylor, and R. McEachern of LLNL.

REFERENCES

1. S. HAAN, *et. al.*, "Increasing Robustness of Indirect Drive Capsule Designs Against Short Wavelength Hydrodynamic Instabilities," *Phys. Plasmas* **12**, 056316 (2005); S. HAAN, *et al.*, "Update on Specifications for NIF Ignition Targets, and Their Rollup into an Error Budget," *Fusion Sci. Technol.* **49**, 553 (2006); S. W. HAAN, *et al.*, "Update on Specifications for NIF Ignition Targets," *Fusion Sci. Technol.*, this issue.

2. E. I. MOSES and C. R. WUEST, "The National Ignition Facility: Laser Performance and First Experiments," *Fusion Sci. Technol.* **47**, 314 (2005); G. H. MILLER, E. I. MOSES, and C. R. WUEST, "The National Ignition Facility," *Opt. Eng.* **43**, 2841 (2004).

3. B. W. MCQUILLAN, A. NIKROO, D. A. STEINMAN, F. H. ELSNER, D. G. CZECHOWICZ, and M. L. HOPPE, "The PAMS/GDP Process for Production of ICF Target Mandrels," *Fusion Technol.* **31**, 381 (1997).

4. R. MCEACHERN, C. ALFORD, R. COOK, D. MAKOWCKI, and R. WALLACE, "Sputter-Deposited Be Ablators for NIF Target Capsules," *Fusion Technol.* **31**, 435 (1997).

5. H. W. XU, A. NIKROO, J. R. WALL, R. DOERNER, M. BALDWIN, and J. H. YU, "Be Coating on Spherical Surface for NIF Target Development," *Fusion Sci. Technol.* **49**, 778 (2006).

6. M. MCELFRESH, *et al.*, "Fabrication of Beryllium Capsules with Copper-Doped Layers for NIF Targets: A Progress Report," *Fusion Sci. Technol.* **49**, 786 (2006).

7. H. W. XU, *et al.*, "Beryllium Capsule Coating Development for NIF Targets," *Fusion Sci. Technol.*, this issue.

8. R. MCEACHERN and C. ALFORD, "Evaluation of Boron-Doped Beryllium as an Ablator for NIF Target Capsules," *Fusion Technol.* **35**, 115 (1999).

9. A. F. JANKOWSKI, M. A. WALL, and T. G. NIEH," Crystallization of Beryllium-Boron Metallic Glasses," *J. Non-Cryst. Solids* **317**, 129 (2003).

10. S. BAJT, *et al.*, "Oxidation Resistance and Microstructure of Ruthenium-Capped Extreme Ultraviolet Lithography Multilayers," *J. Microlithogr. Microfabr. Microsyst.* **5**, 23004 (2006); S. BAJT, *et al.*, "Improved Reflectance and Stability of Mo-Si Multilayers," *Opt. Eng.* **41**, 1797 (2002).

11. J. P. ARMSTRONG, A. M. RUBENCHIK, J. GUNTHER, and B. C. STUART, "Micron Scale Deep Hole Drilling for Beryllium Capsule Fill Applications," *Fusion Sci. Technol.* **49**, 823 (2006).

12. R. C. COOK, S. A. LETTS, S. R. BUCKLEY, and E. FEARON. "Pyrolytic Removal of the Plastic Mandrel from Sputtered Beryllium Shells," *Fusion Sci. Technol.* **49**, 802 (2006).

13. C. TOMASTIK, W. WERNER and H. STORI, "Oxidation of Beryllium - A Scanning Auger Investigation," *Nucl. Fusion* **45**, 1061 (2005).

14. S. A. LETTS, E. M. FEARON, S. R. BUCKLEY, M. D. SACULLA, L. M. ALLISON, and R. COOK, "Fabrication of Polymer Shells Using a Depolymerizable Mandrel," *Fusion Technol.* **28**, 1797 (1995).

15. E. L. ALFONSO, J. S. JAQUEZ, and A. NIKROO, "Gas Permeation Barrier Characterization by Mass Spectrometry," *Fusion Sci. Technol.* **49**, 773 (2006).