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This is a preprint of a paper to be presented at the 17th ANS Topical Meeting on the Technology of Fusion Energy, November 13-16, 2006, in Albuquerque, New Mexico, and to be published in *Fusion Sci. and Technol.*

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Work supported by
the U.S. Naval Research Laboratory
under N00173-06-C-6005

GENERAL ATOMICS PROJECT 30266
DECEMBER 2006

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THE CHALLENGE OF AN IFE FOAM CAPSULE OVERCOAT

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The baseline design for the laser-driven Inertial Fusion Energy (IFE) target is a 4.6 mm foam capsule with a polymer overcoat of 1 to 5 μm. The specifications for this overcoat include surface finish, permeation properties, uniform wall thickness and conformal coating of the foam shell. Many of these specifications are not unlike the full density polymer National Ignition Facility targets, but the foam shell adds to the fabrication difficulty. Since the foam surface is composed of open cells, creating the overcoat by typical vacuum deposition processes would start by replicating the foam surface making it very difficult to achieve the required surface specification. Instead an overcoat is made using interfacial polymerization at the edge of the foam surface. This is done by filling the foam shell with an organic solvent containing one reactant, then placing the shell into water containing another reactant. The reaction occurs only at the interface of the two solutions.

This technique was pioneered at the Institute of Laser Engineering (Osaka University) with 0.8 mm diameter methacrylate shells.[1] The process was later extended to 0.9 mm diameter resorcinol-formaldehyde and divinyl benzene (DVB) shells.[2,3] For the High Average Power Laser Program target we need to extend the process to 4.6 mm diameter DVB foam shells. The properties of the DVB foam and the larger diameter of the shell make it more difficult to produce a gas tight shell. This report will explain how we are adapting the process and the results to date.

I. INTRODUCTION

The High Average Power (HAPL) program is tasked with exploring the path to producing electricity for the consumer by using extensions of current technologies. The effort is cooperative across several disciplines with the approach being to develop synergetic designs of the system components including, but not limited to, the driver, target, target injection, and chamber wall.[4]

The baseline target is a 4.6 mm OD foam shell (density 100 mg/cm^3) with a polymer overcoat which is in turn covered by a thin metallic coating.[5]

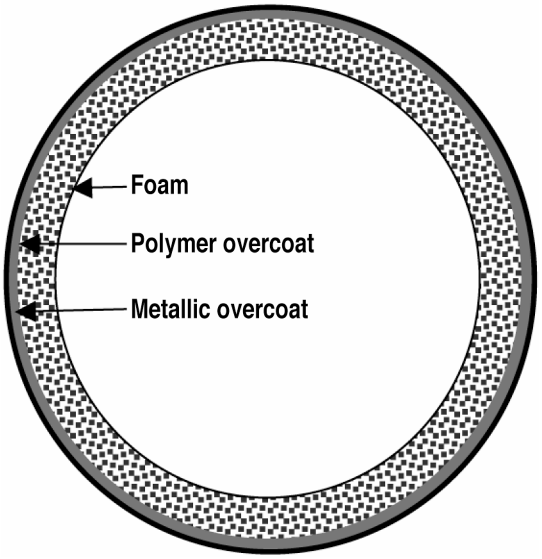

Fig. 1. This is the baseline target. The foam wall is 176 μm thick, the polymer overcoat is 1–5 μm thick and the metallic overcoat is 0.08 μm thick.

The target fabrication must allow for mass production since 500,000 targets will be needed per day. We begin the fabrication by creating the foam shell using microencapsulation techniques – a technology heavily used for mass production in pharmaceuticals. While our process is the same as a typical commercial process, the fabrication of the foam shell is given added precision by being formed by a triple orifice able to precisely control flow rates setting exact size and wall thickness.

The foam system is polymerized from the monomer divinyl benzene and was invented by the author to meet the needs of the HAPL program.[6] The foam specifications were for a pure hydrocarbon foam (no elements other than carbon and hydrogen) that could be made in the density range of 20 to 100 mg/cm^3 and have a cell size of a micron or less.

After the foam shell is polymerized, a polymer overcoat is placed at the outer edge of the foam, the overcoated foam shell is dried by super critical CO$_2$, and a thin metallic layer is applied. After the metallic coating, the target is filled with deuterium and tritium, cooled to cryogenic temperatures, the fill is uniformly layered, and the target injected into the chamber center.

Our effort is to develop the processes and show proof of principle for the shell production up to the point of fill; i.e. fabricate the foam shell, the polymer overcoat and metallic overcoat. Of the three layers, it is the polymer overcoat that has proven to be the most challenging to reproducibly fabricate.

II. DISCUSSION

The polymer overcoat has four requirements: (1) must be conformal with the outer edge of the foam shell, (2) must be 1 to 5 μm thick and of uniform thickness, (3) must be able to retain the gas fill, and (4) must have a surface finish of less than 50 nm RMS.[5] The foam substrate precludes the use of the typical vapor deposition coating techniques. Those techniques would begin by replicating the surface of the foam which is composed of ~ 1 μm open cells. The resultant surface finish would almost certainly exceed the 50 nm specification.

The technique we are pursuing is interfacial polymerization. Like the foam shell fabrication process, the interfacial polymerization is a commercial micro-encapsulation process. It had previously been used by the Institute of Laser Engineering in their initial work to form an overcoated foam shell for fusion research.[1] To form the overcoat, the foam shell is filled with a solvent containing an organic acid chloride. This foam shell is immersed in an aqueous phase that contains polyvinyl phenol (PVP). The pendant OH groups of the PVP react with the acid chloride to form an ester (with the release of hydrochloric acid), but only at the water-solvent interface. This interface is at the outer edge of the foam since the foam was completely filled with the solvent solution. Thus the coating forms by replicating the spherical solvent drop rather than replicating the foam structure.

To produce 0.9 mm resorcinol-formaldehyde foam shell overcoat, Nikroo *et al.* found that this PVP-acid chloride technique had ~ 90% yield of gas tight shells.[2] Using 0.9 mm DVB shells Paguio *et al.* found that PVP coated shells had a yield of gas tight shells of ~ 50%.[3] They achieved a higher yield by using a two step coating: the PVP-acid chloride coating followed by plasma polymer (GDP). The two step approach was developed after they noted that PVP coatings of 3 μm or more showed 20% shrinkage. This shrinkage compressed the foam shell. They also noted that thin (~ 1 μm thick) coating did not shrink, but also did not retain a gas fill. The combination of a thin PVP wall and a GDP overcoating gave a ~ 5 μm thick polymer wall with a yield of 70% gas tight shells.

III. RESULTS

To produce the 4.6 mm target we anticipated that the two step coating approach would be successful. The PVP wall was fabricated, dried and coated with GDP. Unfortunately, the percentage of shells that were gas tight was very small. Furthermore, making thicker PVP layers or adding thicker GDP coatings did not always make the shells gas tight (Fig. 2). The acceptable wall thickness limit (≤5 μm) is shown on the graph as a dotted line.

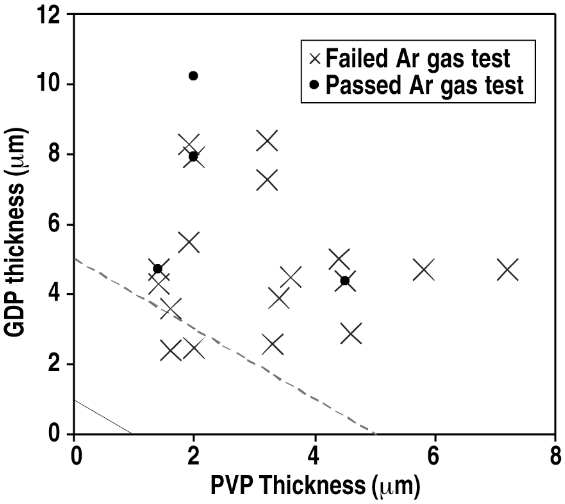

Fig. 2. Argon pressure test results. To determine if a shell could hold gas it was filled with argon and then tested for argon fill using x-ray fluorescence. If no argon signal was present it was because the shell was unable to hold the fill. Each data point actually represents several shells.

We hypothesize that the reason for the failure of the PVP-GDP overcoat is that there are small (1 μm or less) cracks in the PVP coating. We know from experience that a thin GDP layer cannot seal a micron sized gap. We also noted that the surface finish of the shells that failed to hold gas often had surface finishes of approaching 1 μm RMS. We see two possible sources for the cracks: pressure differences across the overcoat or dimensional differences.

III.A. Pressure Differences

The failure of the gas tight coating may be a result of stress on the overcoat due to pressure differences across the shell wall. There are two modes in which a shell can fail due to pressure, burst or buckle. In both modes, a larger shell has more stress. For a thin walled sphere in the burst mode the stress is:

$$\sigma = \frac{\Delta \mathrm{Pr}}{2\mathrm{t}} \qquad (1)$$

Where

σ = stress
ΔP = pressure across the wall
r = radius
t = wall thickness

For a given pressure and wall thickness, the stress on a 4.6 mm OD wall is 5 times the stress on a 0.9 mm OD wall.

An analysis of the buckle pressure of overcoated foam shells was done at Los Alamos National Laboratory.[7] For a thin walled sphere in the buckle mode, the pressure difference across the wall that will cause collapse is:

$$\Delta P = \frac{2E}{\sqrt{3(1-v^2)}}\left(\frac{w}{r}\right)^2 \qquad (2)$$

Where

E = the modulus of elasticity of the layer material
w= thickness of the supporting layer
r = radius of the sphere
V = Poision's ratio.

Thus the buckle pressure is a function of r^2, but for external pressures the overcoat is assumed to be supported by the foam layer in the LANL work. They found the buckle strength of the polymer overcoat "is more than an order of magnitude less than the strength of the foam shell at a foam density of 20 mg/cm^3." The IFE foams are 100 mg/cm^3. The elastic modulus is related to the density by the following relationship:

$$E = C\rho^n \qquad (3)$$

Where

C = a proportionality constant
ρ = foam density
n = a correction for the morphology of the foam, determined to be 2 in the reference quoted.

This indicates a 100 mg/cm^3 foam would be 25 times stronger than the 20 mg/cm^3 foam and at least 250 times stronger than the polymer overcoat. This would seem to indicate that buckling should not be a concern, but that may not be true. If our assumption that the overcoat is not gas tight because of micron sized cracks, then there is the possibility that these cracks are occurring in the overcoat where it spans the micron sized cells of the foam.

It must be clarified that it is the thin PVP overcoating that is exposed to the stresses. (The GDP coating is added after the PVP overcoated foam shell is dried and dimensionally stable.) The post polymerization steps are: a 10% hydrochloric acid rinse (designed to improve surface finish), exchange of the internal solvent phase for isopropanol, which is in turn exchanged for liquid carbon dioxide. These steps introduce osmotic pressure changes.[8] To demonstrate this, we fabricated simple PVP-acid chloride shells (with no foam shell underneath) and studied the wall microscopically during solvent exchanges. The shell shows dimpling due to the osmotic pressure difference.

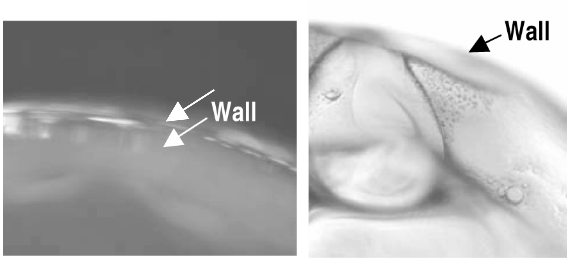

Fig. 3. The left hand figure shows the PVP-acid chloride wall as made. The photo on the right shows the same shell dimpled due to an osmotic pressure difference. (100×)

After the solvent exchanges, the shell has liquid CO_2 on the inside and outside. The pressure vessel is then heated, to send the CO_2 to a supercritical state so as to eliminate capillary forces damaging the foam in the subcritical state. This heating increases the pressure (both inside and outside the shell) from 5 MPa to 9 MPa. Pressure differences across the overcoating wall could be present, due to temperature gradients across the wall, or due to incomplete solvent exchange with some residual isopropanol remaining inside the shell wall. Lastly, a vent of the supercritical CO_2 that is too rapid can develop a pressure difference across the wall. The entire process of solvent exchange and supercritical CO_2 drying presents several opportunities for pressure gradients across the overcoat wall.

III.B. Dimensional Differences

The other possible source of the cracking is a dimensional mismatch between the foam shell and the PVP overcoat during the supercritical point drying. If the overcoat shrinks significantly more than the foam it will be stressed beyond its limit and the overcoat will rupture. Indeed there are cases where that appears to be a plausible mechanism for failure (Fig. 4). It was already noted in the overcoating work of 0.9 mm shells, that PVP coatings thicker than 3 μm have noticeable shrinkage. It was thought that at a 1 μm or less there was no shrinkage, yet in our work with large shells even thin coatings can have large cracks. The shrinkage of thin PVP coatings may not have been noted in the previous work since a small change in the size of a coating on a small shell may not have been easily detectable. The larger diameter shell may be demonstrating that even the thin PVP coatings have some shrinkage, and this shrinkage is greater than the DVB shrinkage.

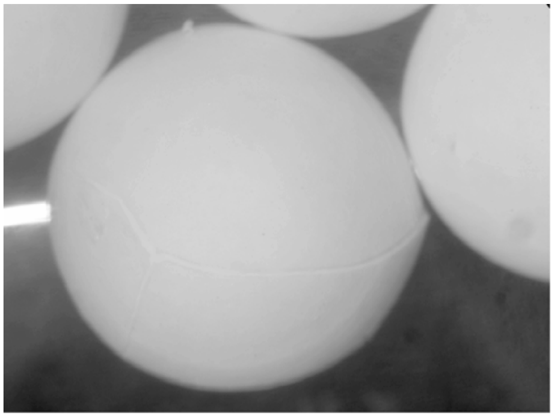

Fig.4. his photo shows an overcoat that appears to have shrunk more than the underlying foam shell.

The 100 mg/cc DVB foam does experience shrinkage of a few percent. This is minimal but as the diameter of the foam shell increases this percentage becomes significant (A 3% shrinkage would be about 140 μm). We explored the relationship of foam shrinkage to radical initiator, polymerization solvent and polymerization conditions by casting rods ~ 20 mm in length and 7 mm in diameter. The rods were measured after solvent exchanges and after drying. All of the formulations had swelling in a good solvent (xylene), shrinkage in a poor solvent (isopropanol) and shrinkage in the drying (Fig. 5).

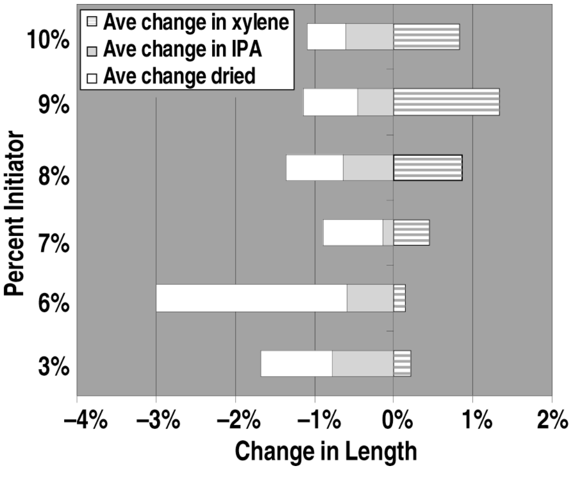

Fig.5. This is a subset of the experiments done to explore the dimensional stability of the DVB foam cast in rods at 100 mg/cc. The total change for a given foam ranged from 1.4% to 3.2%

There is the possibility that the shrinkage of the PVP at various thicknesses could be accurately determined. If the PVP overcoating thickness and the processing conditions of the DVB polymerization could be precisely controlled, the shrinkages could be matched. However, this seems a difficult task to do in a mass production scenario.

IV. FUTURE WORK

Given that this report is of a work in progress, there is much future work. We are going to try slight modifications of the reactants of the interfacial polymerization. By changing the reactants we can (1) change the osmotic pressure by changing the solvent exchange rates, and (2) change the shrinkage of the overcoat possibly correcting dimensional mismatch. See Table 1 for the list of reactants that are being tested.

TABLE I. Reactants

Water Reactant	**Organic reactant**
PVP	Isophthalyol Dichloride
Polyvinyl Alcohol	Isophthalyol Dichloride
Polyvinyl Alcohol	Sebacoyl Chloride
Polyvinyl Alcohol	Benzoyl Chloride
Melamine-formaldehyde	None
Resorcinol	Isophthalyol Dichloride
Hydroxyethyl Cellulose	Isophthalyol Dichloride

PVP and isophthalyol dichloride are being included as our reference point to the previous work. Several thicknesses of this coating will be tried. Polyvinyl alcohol (PVA) is being used in five different molecular weights. This allows us to determine the effect of molecular weight, especially notable with the mono-functional benzoyl chloride. (We are not able to do any molecular weight comparisons with PVP as it is commercially available in only one molecular weight.) Another reason for choosing PVA is that it is known to be a good hydrogen barrier. The melamine-formaldehyde is not an interfacial polymerization as such but rather a condensation reaction that deposits the polymer at the solvent interface. That reaction is noted in the literature as producing a very smooth surface finish.[9] The resorcinol and hydroxyethyl cellulose reactants are also noted in the literature, the HEC reaction being mentioned in the ILE paper as a viable candidate. Sebacoyl chloride was chosen for its aliphatic chain and in our preliminary work the resultant polymer shows crystalline structure; crystallinity can give a polymer additional strength. Benzoyl chloride was chosen because it is mono-functional. The benzoyl chloride and the melamine-formaldehyde polymers will not be crosslinked and as such they are expected to have the greatest elasticity allowing them to adapt to the dimensional changes of the foam. With any of these reactants a GDP coating is possible if additional thickness is desired.

For each of these overcoatings the surfaces will be examined by confocal microscopy, before and after CO_2 drying, and those with the smoothest surfaces will tested for gas retention with and without a GDP layer. Also, a new apparatus is being designed to limit the pressure gradients across the shell wall during the CO_2 drying process.

IV. CONCLUSION

Mass producing an overcoat on a 4.6 mm foam shell meeting the HAPL specifications has proven to be difficult. We are addressing issues of a gas tight polymer overcoat, and while not discussed in this report, surface finish specifications are also yet to be met. The final goal must be a process that can yield 500,000 targets per day, so we do not have the luxury of a low yield process followed by thorough sorting processes. We do have a set of planned experiments that hold much promise and will report on that work in the future.

ACKNOWLEDGMENTS

The authors would like to acknowledge the support and funding of this work by the Naval Research Laboratory through contract N00173-06-C-6005.

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