NEW DEVELOPMENTS IN GLASS SHELLS FROM SiGDP — RESIDUAL GASES, GAS FILLING AND TAILORED HALF-LIVES

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Progress has been made in reducing and quantifying residual gases in shells manufactured by the silicon doped glow discharge polymer (SiGDP) to glass process. Previously, glass shells were made using a high temperature, open-air box oven. If the temperature profile used was sufficient, clear, colorless shells were obtained which had ~1/3 of an atmosphere of residual gas consisting of a mixture of N_2, O_2, CO and CO_2 with generally N_2 and CO_2 being the major constituents. Improvements to the process were made by utilizing a controlled atmosphere, high temperature oven and developing an improved temperature profile for the SiGDP to glass conversion process. It is now possible to manufacture clear, colorless glass shells containing noble gas(es), which is a first for the ICF program. In addition, the improvements in our process has led to shells containing less residual gas (N_2, CO, and CO_2) than previously obtainable. Tailored deuterium half-lifes are also possible by adjusting the final sintering temperature which results in glass that is very near but not full density which allows in some cases for fielding of glass shells with half-lives which can be more suitable to the experimentalist.

I. INTRODUCTION

The method for producing glass shells from silicon doped GDP (SiGDP) has been presented previously.[1,2] In step one, silicon doped GDP is deposited on poly(α-methylstyrene) (PAMS) shells. In step two the shell is pyrolyzed at about 300°C in an inert gas, such as nitrogen or argon, to remove the PAMS. In the final step, the silicon doped GDP shell is pyrolyzed in a controlled atmosphere oven (containing oxygen with or without a noble gas) to convert it into a glass shell.

Recent advances in making glass shells by this process include: ability to fill shells with a noble gas; adjusting permeability to better meet desired target characteristics; and a reduction in trapped residual gases and carbon generated during the conversion of the SiGDP to glass.

II. EXPERIMENTAL

All beginning PAMS mandrels were made by the droplet generator technique. All shells were roll coated in a plasma polymerization system based on a helical resonator and piezo bouncer described by previous authors.[3,4] Tetramethyl silane (TMS), trans-2-butene (T2B) and hydrogen were used as feed-stock gases for the plasma coater. The PAMS mandrel was removed after the SiGDP coating step was completed in a controlled heating process in which the temperature was slowly ramped to 300°C under nitrogen (or argon) to decompose and volatilize the PAMS polymer. Table I shows the pyrolysis parameters for the PAMS removal step.

Table I. PAMS Removal in Argon Atmosphere

Temperature Ramp (˚C)	Ramp Rate (˚C/min)	Hold Time at Max ˚C (h)
20–200	10.0	0
200–240	0.1	10
240–260	0.1	10
260–280	0.1	10
280–300	0.1	20

Thermogravimetric analysis (TGA) of the SiGDP to glass process for the conversion of the silicon doped GDP to SiO_2 is shown in Fig. 1.

Inspection of the TGA spectrum reveals the temperature region around 450˚C is where rapid conversion of the carbon and hydrogen into CO_2 and water with concomitant formation of SiO_2 occurs. It is also observed that if the SiGDP is heated to temperatures nearing 600˚C before this conversion process is complete the resulting shells are black in color due to appreciable carbon content in the glass. Based on TGA results, which show a relatively rapid conversion

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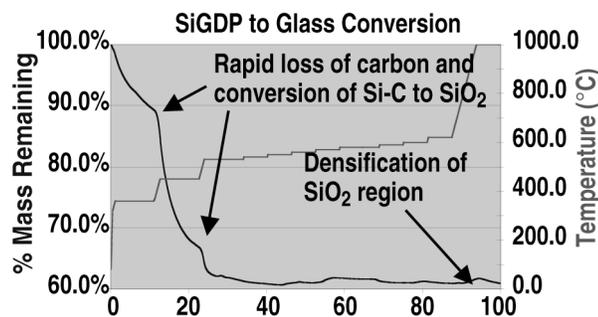
Figure 1. Percent mass remaining as a function of time and temperature during the conversion of SiGDP to glass.

rate at 450°C, this temperature was chosen as the optimum for the conversion of SiGDP to SiO_2.

Although the removal of carbon and apparently the pickup of oxygen is essentially complete by 600°C, the glass shell at that temperature is not yet at full density. The shells generally shrink another percent or two in diameter (without loss of mass) when heated to 1000°C. Also, the permeation properties of the final shells vary depending on the final temperature and hold time.

Permeation experiments were conducted using deuterium (D_2). The deuterium gas was permeated into the glass mandrels by heating them in a sealed, pressurized vessel to 260°C. The outgassing rate (at room temperature) of D_2 was monitored by interferometry or by mass spectrometry. Shells on occasion were crushed in our shell crushing station to accurately determine total internal pressure, residual gas content, and the corresponding half-life as well.

III. RESULTS AND DISCUSSION

The critical variables we can adjust to control the final properties of the glass shells, which include color, permeability, strength and residual gas content, are the temperature ramp/soak profile and SiGDP to glass pyrolysis atmosphere. We have not yet tried adjusting the O_2 pressure in the pyrolysis oven during the conversion process but instead have focused on making adjustments in the temperature ramp/soak profile while keeping the oxygen concentration inside the oven the same from run to run. It may be possible to shorten the length of time it takes to convert the SiGDP to clear, fully dense glass (currently is about a week) if we develop temperature profiles using elevated oxygen pressure. We intend to investigate this possibility at some point in the future.

III.A. Color (Carbon Contamination)

Thermogravimetric data on the conversion of SiGDP to SiO_2 (Fig 1) indicates that the mass of the sample does not change significantly after ~580°C. This agrees well with the observation that in order to make clear, non-colored, glass shells the conversion of SiGDP to SiO_2 must be essentially complete before 600°C is reached. If the SiGDP shells are heated too rapidly in air to 600°C the resulting shells can be anywhere from light brown to opaque and black after the high temperature densification step (sintering from 600°–900°C). This is presumed to be due to incomplete combustion of the carbon present in the SiGDP and resulting incorporation into the densified glass.

The effect of residual carbon on shell properties, such as strength and permeability, has not been systematically investigated yet. However, the colored glass shells that have been measured for deuterium half-life have a somewhat higher permeability (shorter deuterium half-life) than corresponding colorless glass shells.

We have been adjusting the pyrolysis profile based on our TGA results by increasing the hold time at 450°C. Generally, if we hold the shell long enough at 450°C in an oxygen containing environment we will obtain colorless glass shells after the high temperature densification step. We find that a hold time of only 12 h generally results in a very light, yellowish shell, while times in excess of 48 h are generally required to obtain colorless shells.

III.B. Residual Gas Pressure and Composition

Up until five years ago we only had the capability to measure gas pressure inside a capsule by crushing it while immersed in a viscous fluid (glycerin typically). This technique, while generally not used anymore, does have the advantage of providing visual evidence in the form of bubbles from which the total gas pressure inside the capsule can be easily determined. In the gas of glass shells made from the SiGDP to glass process, the entrapped gas generally consists of a mixture of CO and CO_2.

About five years ago we constructed a shell crusher station that allowed us to more easily and more accurately measure high-pressure fills. The shell crusher station consisted of a small, calibrated volume connected to a turbo pump and an MKS 10 torr high precision Baratron gauge. The internal gas pressure of a shell is determined by crushing it inside the calibrated

volume and measuring the resulting pressure rise in the system using the gas law $P_1V_1=P_2V_2$ and correcting for non-ideal gas behavior as necessary for higher pressure fills (100 atm DD for example). The measurement limit for gases inside a shell is a function of shell diameter. A 1mm ID shell has pressure measurement resolution of 0.007 atm for total pressure using our crusher/mass-spec station.

We recently attached a mass spectrometer to the shell crushing station which allows us to determine composition of the gas(es) in addition to the total pressure. Our mass spectrometer is set up to continuously monitor the partial pressure of gases inside the sample chamber, therefore gases prevalent in the atmosphere will be observed as high background pressures in the mass spectra (N_2 and O_2). The CO_2 background pressure is also relatively high because it is generated by processes in the mass spectrometer itself. Unfortunately, CO and N_2 both have the same molecular weight and so is not resolved by the mass spectrometer, resulting in what appears to be a high CO background pressure in the spectrum with the result being a much reduced sensitivity for CO relative to gases like He, Ar, Kr or Xe. The mass spectral detection limit varies depending on molecular weight of the gas as well as whether it is present at appreciable background pressure inside the instrument. The minimum detectable limit for CO and CO_2 inside a 1 mm ID shell is ~0.01 atm and 0.005 atm respectively. The CO_2 detection limit is lower because nitrogen gas has the same molecular weight as CO and results in an increased background for CO.

After collecting the signal for the chamber partial pressures for a sufficient length of time to establish a steady, reliable background for each gas of interest, the shell is crushed inside the chamber and the gases released are measured. Figure 2 shows a mass spectrum of the gas contents of a glass shell crushed using our shell crusher/mass spectrometer station at ~t = 65 s. Only the signals for CO_2 and N_2/CO increased after the shell was crushed. Since N_2 has been eliminated as a possible gas present inside the shell by controlling the pyrolysis atmosphere, it is therefore assumed the increase in the N_2/CO signal is from CO only.

Minimizing the total amount of residual gas present inside a glass shell generally follows the minimization of the color. This makes sense since oxygen needs to permeate inside the shell during the pyrolysis in order to oxidize the carbon. If oxygen can permeate in then the gases formed (CO, CO_2 and water) should be able to permeate out. Table II shows the results of

experiments to minimize the total residual gas content. We have been able to produce shells with total residual gas content <0.1 atm. In general, the only residual gases at sufficient pressure to be detected inside our glass shells are CO, CO_2 and sometimes a small amount of oxygen. Some may wonder why water vapor is not mentioned as a residual gas since it is a product of the conversion process. While water is sometimes observed in the glass shells, it is permeable thru the glass wall at high temperature and so is readily removed and therefore not considered in this context to be a residual gas left inside the shell.
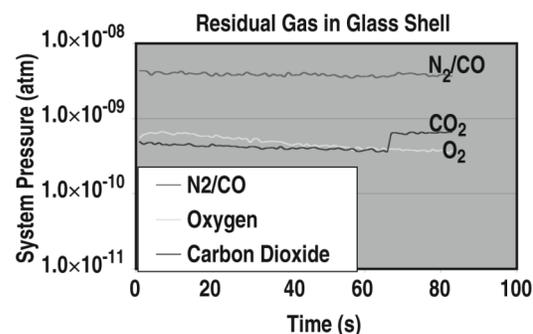
Figure 2. Mass spectrum of a shell containing only residual combustion gases. Shell crushed at ~t = 65 s. Only a small amount of CO_2 (~0.2 atm) and a trace of CO were observed.

Table II. Residual Gas Pressures Minimized by Increasing Hold Time at 450°C Prior to Sintering to 940°C

Shell OD (μm)	Shell Wall (μm)	Pyro Time at 450°C (h)	Resid. CO (atm)	Resid. CO_2 (atm)	Total (atm)
1082	5	60	0.01	0.18	0.19
1123	5	60	0.02	0.17	0.18
1126	5	60	0.02	0.15	0.17
1106	5	100	0.01	0.04	0.04
1115	5	100	0.01	0.04	0.04

III.C. Dopant Gas Fills

Glass shell when fully densified are impermeable to gases such as Ar, Kr and Xe. Prior to the development of the SiGDP to glass process no one has successfully been able to fill a glass shell with a noble gas (other than He) for use in the ICF program. We have successfully entrapped noble gases inside of glass shells by utilizing a controlled atmosphere high temperature oven for the SiGDP to glass conversion process. The oven is pressurized with a mixture of oxygen and helium along with the desired dopant gas prior to beginning the ther-

mal conversion process. Currently the oven needs to be pressurized with ~ a 30% over-pressure of the desired dopant gas in order to achieve the desired final pressure inside the glass shell. Unfortunately, filling glass shells with such gases also requires changes to the temperature profile for the glass conversion process in order to obtain colorless, low residual gas content, glass shells. Figure 3 shows the mass spectrum acquired from a ~900μm diameter glass shell manufactured to contain ~ 0.01 atm Kr and 0.1 atm Ar.
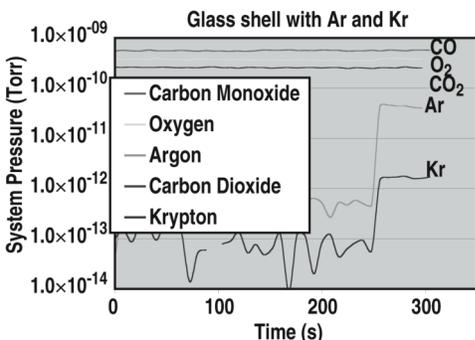
Figure 3. Mass spectrum of gas inside a shell manufactured to contain ~0.01 atm Kr and 0.10 atm Ar. Shell crushed to release gas at ~t = 260 s.

III.D. Permeation

The literature value for the permeability constant K for deuterium through amorphous silica is 2.67×10^{-20} (mol•m)/(m²•s•Pa).[5] The permeability constant K for deuterium found previously for drop-tower produced glass mandrels is 3.0×10^{-20}.[6] Generally, the deuterium permeation constant K of shells made by this process, when sintered to full density at 940˚C, is also consistent with the accepted literature value. However, K can also be made to vary significantly resulting in much higher permeability if desired. This allows the deuterium half-life to be better tailored to the occasional experiment where the full density half-life is too short to allow for target handling and processing time (which may take several days) but too long for practical filling of the target after assembly. Measurement of the deuterium half-life and corresponding K values for a series of shells sintered to different final temperatures are shown in Table III.

III.D. Future Development

Diamond shells have been identified as potentially useful for ICF targets because of their very high strength, attractive density and low atomic number. We have discovered it is possible to pyrolyze SiGDP

mandrels to 900˚C in an oxygen free atmosphere resulting in shiny, black shells. Based on the final shell mass and assuming there is no significant loss of silicon during the pyrolysis we estimate that this shell is 20%Si and 80%C. These shells may potentially be of interest because they are possibly intermediate in properties between glass and diamond. These shells with an average Z of 7.6 are somewhat higher Z than diamond (6.0) but lower average Z than glass (10.0) and appear to be relatively easy to make and should be free of residual trapped gas(es) since they are pyrolzed in vacuum. We intend to investigate the permeation and strength properties of some shells produced in this method to determine if they have potential for use as ICF targets.

Table III. Permeability of SiGDP Produced Glass Shells at Various Sintering Temperatures

OD (μm)	Wall (μm)	K (mol•m/ (m²s Pa)	Sintering Temp (˚C)	DD 1/2 Life (Days)
~250	8	2.3×10^{-20}	940	50
~250	8	8.5×10^{-20}	920	11
~250	8	5.2×10^{-19}	820	1.8

Literature value for deuterium thru SiO_2 is 2.7×10^{-20}

In another development, while it previously has not been possible to manufacture ≥2 mm diameter glass shells with very thin walls (≤5 μm), generally due to destruction of the mandrel during the PAMS pyrolysis step, we have successfully made a glass shell 2150×3.3 μm by laser drilling a ~15 μm hole into the precursor SiGDP shell prior to the PAMS removal step. Providing a pathway for ready removal of the PAMS during the pyrolysis instead of allowing it to diffuse through the thin SiGDP layer results in intact mandrels. The advantages of having the small hole in the glass shell is it assures there are zero residual gases and allows for any type of gas fill. We will continue a few trial runs as time allows to determine how well these shells maintain sphericity and surface finish.

ACKNOWLEDGMENT

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