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November 11, 1977

MAILED

University of California
Lawrence Livermore Laboratories
P.O. Box 808
Livermore, CA 94550

Attention Mr. William H. Chapman
Mail Stop L122

Dear Bill:

SANL-507/020

Enclosed is our final report on the subject SANL. You will note that in spite of the relatively short period of performance, encouraging results were obtained. I hope to be at LLL toward the end of the week of November 14 to discuss this work with you.

In the meantime, we appreciated the opportunity to pursue this interesting work and hope that we will be able to further investigate this technology.

Very truly yours,

Hugh D. Hanes, Program Manager
HIP Program Office

HDH:bc

In duplicate

xc: J.Jepson/Special Materials

FINAL REPORT

on

FEASIBILITY DEMONSTRATION OF CONSOLIDATING
POROUS BERYLLIUM/CARBON STRUCTURES

to

MASTER

UNIVERSITY OF CALIFORNIA
LAWRENCE LIVERMORE LABS

by

M.J. Browning
G.E. Hoover
J.J. Mueller
H.D. Hanes, *Program Manager*

November 11, 1977

BATTELLE
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

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EXECUTIVE SUMMARY

A preliminary feasibility study was performed to determine if porous beryllium structures could be fabricated by consolidating beryllium-coated microballoons into a rigid structure. Both carbon and quartz microballoons were used with beryllium coatings produced by either physical vapor deposition (PVD) or "snowball-coating" with fine beryllium powder. HIP and pressureless sintering were the two methods investigated for consolidating the beryllium-coated particles. A low level of effort was also spent to look at means of fabricating an all-carbon structure.

The short period of time available for conducting the investigations necessitated using on-hand or readily available materials. This limited the number of variations that could be investigated and, in some cases, the degree of success achievable. It was possible, however, to demonstrate feasibility in certain tasks and to identify the problems and potential approaches or solutions in others.

In the major effort with carbon microballoons it was shown feasible to produce satisfactory beryllium coatings on the carbon substrate particles by both the PVD and "snowballing" techniques. Further processing of the coated particles, however, met with difficulties relating either to the evolution of carbonaceous gases from the carbonized substrates or from chemical reaction between the beryllium and the substrate during high temperature treatments. The evolution of gas from the carbon microballoons initially prevented successful sealing of the particles in metallic containers to be used for HIP. This precluded evaluation of HIP as a method of consolidation at a desirably low temperature of 1500 F where chemical reactions can be minimized.

The release of carbonaceous gases during sintering treatments at both 1500 and 2150 F appeared to have an adverse effect on the bonding together of the coated particles. The effects of reaction between the beryllium and substrate were clearly greatest when the sintering treatment was at 2150 F. Despite these problems one sintering attempt made on "snowball-coated" particles yielded an apparently sound, bonded sample structure, indicating some potential for achieving bonding by pressureless sintering. No bonding was obtained, however, in sintering of PVD-coated material. Improved substrate material and the use of HIP for consolidation may lead to successful bonding of coated microballoons. Sintering at required high temperatures of the order of 2150 F is considered unfeasible because of the reaction occurring between beryllium and carbon microballoons.

A limited study of coating quartz microballoons showed the feasibility of producing continuous coatings of beryllium by PVD. The coatings, although continuous, were nonuniform in thickness, but this was readily attributable to the undesirably small size of the microballoons available to the program.

In-situ carbonization was evaluated on a cursory basis as a method of fabricating all-carbon structures. Bonded structures were successfully fabricated by direct carbonization of packed particles and with the aid of a carbonizable organic binder. This general approach appears readily adaptable to the fabrication of large-size structures. Although the structures produced were relatively weak, it should be possible to increase the strength through the proper selection of precursor and organic bonding agent.

INTRODUCTION

A preliminary feasibility study was initiated to determine if porous beryllium structures could be fabricated by consolidating beryllium-coated microballoons into a rigid structure. The target specifications were to coat nominally 1-mm diameter microspheres with 0.5-mil beryllium coatings and then bond into a structure. Because of the very short time period, it was agreeable to use existing or quickly-available materials.

The general approach was to apply coatings to carbon or quartz microspheres. Physical vapor deposition and "snowballing" of fine beryllium powder were the two methods investigated. Once the particles were coated, HIP (pressure bonding) and pressureless sintering were to be investigated as methods for consolidating the microballoons. A low level of effort was to be spent to look at means of fabricating an all-carbon structure.

MATERIALS

Microballoon Substrates

Carbon Substrates

Only two types of hollow particle substrates could be obtained for evaluation in this program in view of the time

limitation imposed by essentially a 1-month contract period. The hollow resin beads, called Eccospheres, are manufactured by Emerson Cuming, and were on hand at the initiation of the program.

Two types of Eccospheres were used in this program:

EP-100 - ~1.8 mm in diameter with a 35- to 70- μ m wall thickness and a bulk density of 0.17 g/cm³

X (unidentified) - ~2.2 mm in diameter with a 40- to 100- μ m wall thickness and a bulk density of 0.18 g/cm³.

SiO₂ Substrates

The glass microballons acquired from Emerson Cuming for this program were Type S1 which had an average wall thickness of 1.5 μ m, bulk density of 0.152 g/cm³, and softening temperature of 1000 C. The 149- to 175- μ m size range was removed from the material received for use in the coating experiments.

Beryllium

PVD Coating Source Material

A 15-cm x 30-cm x 0.6-cm beryllium magnetron sputtering PVD target source plate was machined from a pressed powder billet. The material was grade HP 10, from Kawecki Berylco Industries, Inc. The source material was stable during all of the coating studies so it was unnecessary to use the material supplied by Rocky Flats.

Beryllium Powder

The beryllium powder used in the "snowball" coating experiments was 10 μ m in size. This fraction was separated from minus 325 mesh high purity, P-1 beryllium powder which is commercially available from Kawecki Berylco Industries, Inc. The as-received powder typically contains 0.7-percent BeO, 0.15-percent Fe, 0.004-percent Al, 0.003-percent Si and 0.004 Cu. The minus 10 μ m fraction will typically contain a higher percentage of BeO, perhaps of the order of 0.9 to 1.2 percent, as a result of its greater surface area.

EXPERIMENTAL PROCEDURE

Carbonization of Microballoons

Resin microballoons were converted to carbon without agglomeration by using an appropriate heat treatment procedure. This involved the heating of the Eccospheres in a rotating drum from room temperature to ~ 425 C over a period of 2 hr in air and then maintained at that temperature for about 15 hr. The Eccospheres were then cooled, placed in a stationary quartz tube and heated for 2 hr at 1100 C in argon.

After carbonization, the Eccospheres contained a large portion of particles with poor strength, probably due to the non-uniformity in wall thickness from particle to particle. This material was upgraded by selectively crushing the weaker particles and screening out the stronger particles from the debris. Figure 1 shows the structure of a partially carbonized Eccosphere.

PVD Coating Procedure

To deposit beryllium onto carbon and glass microballoons, magnetron sputtering, a physical vapor deposition

250X

FIGURE 1. TWO-LAYER STRUCTURE OF WALL OF
PARTIALLY CARBONIZED MICROBALLOON

(PVD) technique was used. A planar beryllium source, approximately 15 cm by 30 cm by 0.6 cm, was positioned to sputter downward. The flat, solid-state deposition source enabled a vibratory particle manipulator to be placed directly under the source. This arrangement represented the most promising method of depositing the beryllium coating uniformly onto the microballoons.

Figure 2 shows a 24-in. stainless steel vacuum bell jar coating system used in this work. The 5 kw DC magnetron sputtering power supply used is also shown. Figure 3 shows the particle vibrator assembly. A FMC Snytron Model 01 parts feeder is mounted onto the vacuum system base plate. Figure 4 shows carbon microballoons after having been vibrated part of the way up the spiral track. A stop at the top of the track deflected the spheres back down into the pan. Best mixing of the particles is accomplished by leveling the pan, and by careful setting of the voltage to the vibrator coil.

A Vac-Tec Systems, Inc, Model 5C magnetron sputtering head (not shown) was used. A 15-cm by 30-cm by 0.6-cm beryllium target source plate was attached to the sputtering head.

In operation, a magnetically intensified argon gas plasma discharge forms adjacent to the target when voltage is applied. The argon ions bombard the target plate, knocking beryllium atoms free, which subsequently condense onto the particles. The plate is positioned close (5.6 to 7.6 cm) to the vibrating pan, and shields are provided to prevent beryllium vapor from reaching the system components.

Snowball Coating with Beryllium

The carbonized microballoons were coated with 10 μ m beryllium powder by the "snowballing" technique. This involved rolling the spherical particles in a drum with loose beryllium powder while a solution of parawax in carbontetrachloride was sprayed onto the mixture. During the coating process the microballoons were wetted by the liquid spray, causing the beryllium

3807VD

FIGURE 2. 24-INCH STAINLESS STEEL BELL JAR
VACUUM COATING SYSTEM

3806VD

FIGURE 3. MICROBALLOON VIBRATOR MANIPULATOR MOUNTED
ON VACUUM SYSTEM BASEPLATE

3805VD

FIGURE 4. VIBRATOR PAN SHOWING 1-mm CARBON MICROBALLOONS
PART OF THE WAY UP THE SPIRAL RAMP

powder particles to adhere and build up as spraying continued. The equipment for this procedure, which was used on a previous LLL-funded program to develop low-density beryllium (SANL 456), is shown in Figure 5. The snowball-coated microballoons were built up with a coating estimated to be 3- to 4-mils thick at a density of about 30 percent of theoretical. This thickness was much greater than that ultimately desired (0.6 to 1.5 mils at 30 percent density), but it provided a thickness which was considered more suitable for a first-stage feasibility determination. If sintering or bonding were not effective, it then would not be necessary to question whether the poor result was caused by too thin a coating or the result of incomplete coverage of the surface of the microballoon. Figure 6 shows a group of snowball-coated microballoons.

Sintering Set-Up

Pressureless vacuum sintering trials were made on both PVD-coated and snowball-coated microballons at 1500 and 2150 F for a period of 1/2 hr. The results of sintering of the two types of microballoons are discussed later in this report. Because of the relatively high vapor pressure of beryllium, it is necessary to sinter in a closed system to prevent excessive loss during sintering.

The arrangements of components used in sintering the microballoons are shown in Figure 7. In the two arrangements shown the microballoons were held in either a 0.5-in.-diameter beryllia crucible or directly in the beryllium crucible which was contained in a cup-shaped beryllium member with a beryllium cover. In the arrangement shown in (a) the beryllium containers was totally surrounded by graphite; in arrangement (b) the beryllium container was free of a graphite container. These arrangements were used at two different stages of the sintering trails.

FIGURE 5. SCHEMATIC DIAGRAM OF SET-UP USED TO "SNOWBALL" COAT THE MICROBALLOONS

10X

FIGURE 6. CARBON MICROBALLOONS COATED WITH
BERYLLIUM POWDER BY THE "SNOW-
BALLING" TECHNIQUE

(a) Graphite Enclosure

(b) Beryllium-Tantalum Enclosure

RESULTS

Carbonization of Microballoons

Two forms of carbonized microballoons or hollow spherical particles were used in this study. At the initiation of the program an on-hand quantity of microballoons allowed an early start of the experimental activities. These were subsequently found to have been only partially carbonized and consisted of a two-layer structure as previously shown in Figure 1. The outer layer which consisted of a matrix and fiber phase is carbonized while the inner layer is apparently organic in nature. Significant amounts of gas and volatile material were evolved upon heating the microballoons above about 800 C. This caused some unexpected results which negatively influenced the results of the early experiments.

The second form of carbonized balloon was obtained by heating the partially carbonized or uncarbonized microballons in argon to 1100 C. This treatment produced stable, volatile-free microballoons and was found to yield a relatively large percentage of quite fragile material, much weaker than the initial batch of partially carbonized material. The product was satisfactorily upgraded by removing the fragile particles by brushing the microballoons through a screen. The more fragile ones were broken and easily separated from the stronger. Many of the more fragile particles were found to have locally thin walls or walls partially broken away as seen in Figure 8. Figure 9 shows a collection of upgraded microballoons. The presence of fibers in the precursor is evidenced by the surface topography of the carbonized microballoons.

The carbonized microballoons used in the associated studies were estimated to be nominally 2 mm in diameter.

10X

FIGURE 8. AS-CARBONIZED MICROBALLOONS WITH GROUPING
CONTAINING THIN-WALL AND DEFECTIVE PARTICLES

10X

FIGURE 9. GROUPING OF UP-GRADED FULLY
CARBONIZED MICROBALLOONS

PVD Coatings

Three coating runs were made. Two were made using approximately 2.2-mm-diameter carbon microballoons (Type X), and one using 149- to 17- μ m-diameter SiO_2 (quartz) microballoons. In each case, 50 cc of particles were coated.

The first coating run was interrupted at 2 hr, a sample was removed, and the coating deposition rate was determined to be approximately 0.5 μ m per hour. A run time of 20 hr was used to give a total of 10- μ m Be (0.4 mil).

Typical coating parameters for the first run were:

Base vacuum pressure	2×10^{-6} torr
Argon sputtering pressure	5 mtorr
Volts	440 VDC
Amps	5 ADC
Source-to-particle distance	7.6 cm.

Figure 10 shows a sectioned microballoon from the first run. The outer white layer is the beryllium coating with an average measured thickness of 4 μ m. The coating did not adhere well beyond this thickness, possibly because the particles used in the first run were later found to be incompletely carbonized. Outgassing of the spheres as they were heated during coating may have affected adhesion.

For the second run, fully carbonized microballoons were obtained. In addition, the source-to-particle distance was reduced by 2 cm to 5.6 cm and the power was increased to 2700 watts to increase deposition rate. Figure 11 shows 2.2-mm microballoons (Type X) with an average coating thickness of 10 μ m, deposited in 14 hr. In this run there was no apparent outgassing, so the full thickness was applied.

Finally, a coating run was made using 149- to 175- μ m-diameter SiO_2 (quartz) microballoons. Because of the smaller diameter of the SiO_2 spheres, coating thickness was proportionately reduced to 1.5 μ m. Figure 12 shows a section of these coated spheres with an average effective coating thickness of about 2 μ m. None of the particles shown in this figure are

3825VD

213X

FIGURE 10. 4 μ m BERYLLIUM COATING ON 12-mm CARBON MICROBALLOON

3846VD

33538-10-2

213X

FIGURE 11. 7- TO 14- μm BERYLLIUM COATING ON
1-mm CARBON MICROBALLOON

3845VD

34538-11-3

540X

FIGURE 12. 1- TO 3- μm (2 AVERAGE μm) BERYLLIUM COATING
ON 149- TO 175- μm SiO_2 MICROBALLOONS

(Particles not sectioned at major diameter)

sectioned at their major diameter, so they are not indicative of particle size or coating thickness; the variation in diameters between the particles is a result of particles being on different levels. The non-uniformity of these coatings can be attributed to the small size of the spheres. The vibratory particle device as used did not circulate the small particles as effectively as it did the larger spheres in this exploratory work. It is anticipated that this problem could be overcome in any continuation of this effort.

Beryllium-coated Eccospheres prepared as described above were supplied for consolidation studies involving HIP and other sintering techniques. The work performed on applying beryllium coatings to carbon and quartz microspheres has demonstrated the feasibility of the process and additional work would undoubtedly result in better control over uniformity of coating coverage and thickness.

HIP-Related Activities

As a preliminary step to HIP processing of carbon microballoons, experiments were performed to determine the level of isostatic pressurization that the microballoons could withstand. These isostatic pressing trials were performed at room temperature because there is essentially no difference in strength of carbon between room temperature and the planned maximum allowable HIP temperature of 1500 F.

Isostatic pressurization trials were performed with the microballoons encased in rubber. Starting at 100 psi, trial pressings were made in 100 psi increments until there was evidence of breakage occurring among the particles being pressed. Pressing trials were made on both the weak, non-upgraded material and that accepted as representative of good quality microballoons. This study showed that the microballoons of acceptable quality could withstand 200 psi while the non-upgraded ones withstood only 100 psi.

The choice of 1500 F as a reasonable HIP temperature was based on the use of copper as a HIP container material. At 500 F copper should offer little resistance to deformation and consequently would provide a HIP container that would be essentially plastic and that could subsequently be removed by chemical leaching. Because of a Be-Cu eutectic at 1550 F, this temperature was considered to be a prudent upper limit. Also, higher temperatures were not considered for HIP because of the potential of carbide formation through reaction of the beryllium with the carbon substrate.

Copper HIP containers were prepared from 0.008-in. stock for the HIP trials. Because of the relatively low HIP pressure (200 psi) to be used, it was expected that the containers would yield readily under the low pressure at 1500 F. The containers were made 0.5 in. diameter x 1 in. long. Formed, cup-shaped caps were made as closures for the ends. The caps were inserted, forming an edge weld arrangement at the ends of the tubular container body. Welding was performed in an electron-beam welder.

Satisfactory welds were obtained in joining the first cap into the tubular body, but during attempts to seal in the second cap, with the container full of uncoated microballoons, blow out of the molten weld bead continually occurred at the point of final closure. Apparently, the high thermal conductivity of the copper and the resulting heating of the contents caused evolution of gases, and enough pressure generated to disrupt the weld. The problem was greatest with the partially carbonized microballoons. In this case enough gas was generated to blow out the cap before fusion of the copper occurred. This provided the first evidence of the fact that the initial batch of microballoons was not fully carbonized and as a result contained volatile organic material.

The above problem was lessened but continued to exist when fully carbonized microballoons became available. The closure welds could then be made to near completion before sufficient pressure was generated to blow out the final fused section of the weld.

As a consequence of the above welding problems with uncoated microballoons and the expected increase in the problem with the use of parawax-containing snowball-coated microballoons, further work on the preparation of HIP containers was discontinued.

Sintering Studies

Snowball-Coated Microballoons

The initial sintering trials were performed on snowball-coated microballoons which were only partially carbonized. Neither sintering of the powder coatings nor joining together of the particles resulted at either the 1500 F or 2150 F sintering temperatures. In both cases the coated spheres shrunk to about 80 percent their original diameter while retaining their powder coatings. Figure 13 shows a group of particles that were sintered at 1500 F. The major difference between the results at these two temperatures was that of the surface appearance. The specimens treated at 2150 F were whitish in coloration compared with a dull gray color from the 1500 F treatment. In either case the powder coating could be easily broken free from the substrate. The whitish coloration from the higher temperature treatment was believed to result from carbide formation from contact between the beryllium and the rich carbonaceous atmosphere resulting from volatilization of the uncarbonized organic material. Figure 14 shows a section through the wall of a microballoon after its uncarbonized layer was volatilized away during the vacuum treatment.

10X

FIGURE 13. SNOWBALL-COATED MICROBALLOONS
AFTER SINTERING 1/2 HR AT 1500 F

500X

FIGURE 14. WALL OF PARTIALLY CARBONIZED MICROBALLOON
AFTER VOLITIZATION OF UNCARBONIZED INNER
LAYER

Sintering trials at the two temperatures were repeated but on fully carbonized microballoons coated with beryllium powder. The result at 1500 F was similar to that obtained with the partially carbonized microballoons; i.e., no sintering of the coating or bonding together of the coated spheres. The 2150 F treatment, however, did result in joining together of the coated spheres with obvious sintering of the beryllium. Figure 15 shows the joined cluster of microspheres. The metallic appearing surface of the beryllium can be seen where a surface coating formed on the spheres has spalled off. Neither the composition or source of the coating was identified.

The bonded cluster of microballoons was too small and irregular in shape to be tested for strength. Despite the loss of some spheres from the periphery of the cluster, the bonded cluster was found to resist damage during simple handling and squeezing between fingertips.

After obtaining the above result a larger cluster of coated microballoons was sintered to obtain a larger specimen for strength test. In this case the microballoons were placed in the larger beryllium cup (as shown in Figure 7a) with the beryllia crucible removed. Sintering was again performed for 1/2 hr at 2150 F. The result this time was unsatisfactory with no evidence of sintering or bonding having taken place.

A second attempt was made to produce a large bonded specimen with the component arrangement shown in Figure 7b. With this arrangement the graphite is eliminated as a container material to preclude the possibility of carbiding occurring from an exterior source. Tantalum was used to provide a getter for gases released internally during heat-up and sintering. The result in this case was no different than that of the previous trial. The microballoons showed no evidence of bonding, and the beryllium powder was easily broken free of the substrate showing again that sintering had not occurred.

/10X

FIGURE 15. BONDED CLUSTER OF BERYLLIUM POWDER-
COATED MICROBALLOONS SINTERED 1/2
HR AT 2150 F.

PVD-Coated Microballoons

The first trial sintering of PVD coated microballoons was done on those of the initial lot of material which was only partially carbonized. Sintering was performed at 1500 F with the specimen material contained in a beryllia crucible in the arrangement shown in Figure 7a. As in the case of the snowball-coated specimens the PVD-coated particles shrunk in size and no bonding occurred. The result differed, however; the PVD-coated particles developed breaks in their walls. A grouping of the particles after sintering at 1500 F is shown in Figure 16. The microballoons in this view showed clear evidence of their fibrous make up. The surface features of the particles are clearly evident because of the very thin coating present on this first lot of material prepared (0.0002 in.).

Sintering of a second portion of the PVD-coated material at 2150 F resulted in no bonding occurring and similar rupturing of the walls. The particle surfaces were whitish, similar to those of the snowball-coated specimens sintered at 2150 F. A sample grouping is shown in Figure 17.

Mechanically upgraded and fully carbonized microballoons were used in the subsequent evaluation of the PVD coating. Since no particle bonding had been obtained in any of the trials at 1500 F, only the 2150 F sintering temperature was used in a singular sintering trial on this material. The sintering arrangement shown in Figure 7b was used to minimize contamination by carbon. The result was an improvement over that with the partially carbonized particles in that no rupturing of the particle walls occurred; however, no bonding of particles occurred. The particle surfaces again tended to be whitish in coloration but not to the extent that it occurred with the partially carbonized microballoons.

FIGURE 16. GROUPING OF PVD-COATED PARTICLES SINTERED AT 1550 F SHOWING TYPICAL RUPTURING OF THE WALLS FROM INTERNAL GAS GENERATION

10X

FIGURE 17. PVD-COATED AND PARTIALLY CARBONIZED MICROBALLOONS SHOWING WHITE COATING AND RUPTURED WALLS AFTER SINTERING AT 2150 F

Consolidation of Uncoated Carbonized Eccospheres

In addition to the beryllium-coated hollow particle approach to preparing a low-density structure, several exploratory experiments were conducted on consolidating the hollow carbon particles without a beryllium coating. As described above, the hollow carbon particles used as a substrate for beryllium coating were prepared by carbonizing hollow resin (Eccosphere) microballoons. During the course of the carbonization treatment, the resin undergoes several changes in physical states, at least one of which involves a softening which can result in the bonding of one particle to the other if the particles are permitted to remain in contact during this stage.

Accordingly, Eccospheres (Type X), after a treatment of 425 C in air, were packed in a closed-end quartz tube of about 35-mm ID. The packed particles were then heated in argon to 1000 C over a period of about 7 hr, holding for 1 hr at 400, 600, 800, and 1000 C. A handleable but weak cylinder, as shown in Figure 18, was formed with a bulk density of about 0.174 g/cm^3 . The strength of this structure can probably be improved by using inherently stronger Eccospheres and/or modifying the consolidation treatment.

Type EP-100 Eccospheres in a size 1.7 mm to 2.0 mm were placed with no previous treatment in a closed-end quartz tube of about 22 mm ID and slowly heated in argon to 1100 C over a period of 3 hr. A cylinder (Figure 19) resulted from this resin and treatment that had a bulk density of 0.32 g/cm^3 and was stronger than that described above prepared from Type X material. However, its strength was still probably less than desired, but the feasibility of the technique was demonstrated and the strength can probably be significantly improved with further parameter studies.

3843VD

FIGURE 18. CONSOLIDATED UNCOATED PRETREATED
RESIN MICROBALLOONS

3841VD

FIGURE 19. CONSOLIDATED UNCOATED UNPRETREATED
RESIN MICROBALLOONS

3844VD

FIGURE 20. CONSOLIDATED UNCOATED FULLY CARBONIZED
RESIN MICROBALLOONS USING A RESIN BONDING
AGENT

A variation of this consolidation technique was evaluated which offered the possibility of a much stronger structure. This involved the use of a carbonizable resin to effect the bond between the particles. Eccospheres of a size 1.6 mm to 1.8 mm which had been subjected to the carbonization treatment described above were mixed with a phenolic resin, UCAR 15 (product of Union Carbide Corporation). Only enough resin was used to wet the surface of the microspheres. The coated particles were then placed in a closed-end quartz tube and heated in argon to 1100 C over a period of 2 hr and held at this temperature for 1 hr to carbonize the UCAR 15 resin. The cylinder formed is shown in Figure 20 and has a bulk density of 0.170 g/cm^3 . Its strength was considerably better than that of that prepared by sintering preheated Eccospheres without a bonding resin, but less than that prepared by sintering unpretreated particles.

The strength of the resin bonded compact can probably be further improved with the right selection of bonding resin and treatment.

As indicated above, this brief exploration of techniques to consolidate uncoated carbon microballoons into a low-density structure has demonstrated the initial feasibility of the approach but additional work is needed to determine if sufficient strength can be built into the structure while maintaining the low density to meet the requirements of the intended application.

DISCUSSION OF RESULTS

During the conduct of the program, the results were somewhat masked by the outgassing that plagued the experiments with the carbon microballoons. Nevertheless, preliminary evaluation of the processes was possible in this brief study.

First, the instability of the carbonaceous material interfered with the coating. More thorough heat treatment provided a better substrate to accept the PVD coating, but the substrates were still too unstable to be vacuum sealed into a HIP container. It is possible, although unlikely, that carbonaceous gas was present, at least to a limited degree, in all of the subsequent consolidation studies.

Probably the most limiting factor in this study was the reaction between the carbon substrate and the beryllium coatings, both PVD and snowballed. First, the indication of prior work was that 1500 F was approximately an upper limit for the two materials to be compatible in a diffusion mode. However, the presence of a carbonaceous gas could have increased the reaction rate, especially in the snowballed coatings where the surface area of the particles in the coating is much greater. Because the outgassing prevented sealing the microballoons in a HIP container, it was not possible to evaluate whether interparticle bonding could be achieved at these relatively low pressures. Certainly, past work would indicate that the temperature was sufficiently high.

Because of the unavailability of the SiO_2 until late in the program, we were unable to evaluate the stability during consolidation. The quartz microballoons were successfully coated but the small particle size limited the uniformity of the coating thickness. Based on past experience, we could infer that the quartz and beryllium would be compatible in the 1500 F range. The manufacturer reports that 55 percent of the quartz microballoons will withstand a hydrostatic pressure of 1500 psi at room temperature and that the softening temperature of these balloons is 1000 C. It is difficult to extrapolate this data to 1500 psi but it is believed that they would withstand a reasonable HIP pressure.

At the higher temperatures required for pressureless sintering (i.e., 2150 F) it is clear that the beryllium and graphite are not compatible. While there is no experimental evidence to back this, we feel that the same would be true of

the SiO_2/Be couple. The program also confirmed that temperatures in the range of 1500 F are too low to pressureless sinter Be structures. Therefore, it seems unlikely that pressureless sintering of Be-coated spheres, in the absence of some activation technique, would accomplish the desired objective.

Temperature becomes a limiting process factor in bonding Be-coated microballons. The limited compatibility information indicates that 1500 F might be a practical upper limit. As previously stated, this should be sufficient to provide interparticle bonding under sufficient contact pressure. Therefore, the major limiting factor is the mechanical stability of the microballons evaluated. The room temperature isostatic loading of the carbon microballons indicated this pressure to be relatively low. It is probable that a stronger carbon microballoon than that used in this program could have been developed had time permitted. The epoxy resin microballons from which the carbon microballons are prepared were fabricated by building up their outer shell with successive resin layers. Obviously, a stronger particle could result if a resin particle with a thicker shell was used as a precursor. In addition, it was not possible in this brief program to study particle strength as a function of carbonization treatment.

Unfortunately, no data was generated on the quartz, but it is felt that it could be possible to generate a reasonable pressure/temperature "window" in which to pressure-sinter coated microballons.

Assuming an interest in porous graphite structures, the approach briefly explored offers a relatively simple alternative to the beryllium porous structure. Certainly, the techniques demonstrated here could be easily scalable to large structures.

Techniques not investigated because of time limitations, are in-situ vapor deposition processes. CVD infiltration could be an alternative to the processes developed above for an all graphite structure. Transporting beryllium by a vapor transport technique into a packed matrix of microballons could also be

an alternative, although processes of this type are only in the conceptualized stage at this point.

CONCLUSIONS

Based on this preliminary feasibility, the following conclusions can be reached.

1. The feasibility of applying thin beryllium coatings on carbon and quartz microballoons by the PVD process was clearly demonstrated.
2. Pressure bonding of the beryllium-coated microballoons was not demonstrated; however, the compatibility problem is minimal at the normal bonding temperature and it is assumed that bonding is feasible if microballoons of sufficient strength were available.
3. Pressureless sintering of beryllium-coated microballoons does not appear to be feasible primarily because of the excessive reaction at the sintering temperatures.
4. In-situ carbonization is a practical alternative for fabricating an all-carbon structure.

RECOMMENDATIONS

It is recommended that the program be continued with emphasis on three tasks: (1) continue the evaluation of the pressure sintering of Be-coated carbon microballoons, (2) further study of all-carbon porous structures, and (3) initiate an exploratory investigation of a vapor consolidation technique for fabricating a porous structure of microballoons.

In the current program, the pressure sintering approach to preparing a porous beryllium structure was not conclusively evaluated because of problems with the quality of carbon microballoons available. It is suggested that an effort first be made to procure or develop stronger non-outgassing carbon

balloons. If a suitable microballoon can be obtained, then continue with the pressure sintering studies. In addition, the use of a beryllium-coated quartz microballoon should be factored into the sintering studies. The objective of this task would be only to demonstrate the feasibility of the approach and generate small samples for examination. After the suitability of the beryllium structure had been ascertained by LLL, then a follow-on program would be designed to supply larger samples for a more thorough evaluation at LLL.

If an all-carbon structure is considered a suitable alternative for the porous beryllium structure, then an effort on this approach should be directed toward optimizing the carbon balloons, bonding resin, and process treatment to obtain the lowest density structure consistent with a crush strength sufficient for the intended application. This task should result in structures of a size suitable for evaluation by LLL.

The task involving the vapor consolidation of a packed bed of microballoons would be an exploratory study of two approaches. The objective of this study would be to establish if either approach might be used to fabricate a suitable porous structure for the application of interest. One approach would be the consolidation of uncoated-carbon microballoons by depositing carbon in the interstices of a packed bed of microballoons by the pyrolysis of a hydrocarbon such as methane. The other approach would entail the transport of beryllium vapor into a packed bed of beryllium-coated or possibly uncoated-carbon microballoons and cause the beryllium to deposit in the structure by adjusting temperatures. The beryllium thus deposited should bond the individual particles together.

NOTICE

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