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FINAL REPORT

on

FABRICATION OF ULTRA-LOW DENSITY BERYLLIUM

to

LAWRENCE LIVERMORE LABORATORIES
LIVERMORE, CALIFORNIA

December, 1976 ✓

by

John J. Mueller ✓

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Attention Special Materials Staff/
Mr. Collin R. Campbell

Gentlemen:

SANL 456/019

Enclosed is the final report covering the work performed under the referenced SANL. In the research conducted, feasibility of preparing an ultra-low density beryllium structure of desired pore size was successfully demonstrated. We consider the results obtained to be very significant and urge that process optimization work be authorized.

Three copies of the draft report were delivered to Dr. Copeland in December; these should be destroyed. Questions regarding this report and the research should be directed to the Principal Investigator, John J. Mueller at (614) 424-7604. We are pleased that we had the opportunity to serve you.

Very truly yours,

Kenneth E. Meiners

Kenneth E. Meiners
Associate Manager
Materials Application Section

KEM/cmb

cc: Dr. A. Copeland, NEED, LLL
TID, LLL

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SUMMARY

The subject experimental program was directed to determining the feasibility of producing porous beryllium structures of 15 percent of theoretical density with nominal 1-mm-diameter pores by a technique involving the use of evaporable pore-forming filler material. The experimental work carried through from the initial forming of near-spherical particles of evaporable filler materials to the evaluation of fabricated porous beryllium specimens. Naphthalene and ammonium chloride were selected and evaluated for their utility in this fabrication concept. The overall concept involves the following basic steps: (1) forming near-spherical evaporable pore-forming particles, (2) coating these particles with beryllium powder, (3) cold consolidating the composite material into a self-supporting body by isostatic pressing, (4) removing the pore-forming material by its evaporation through the finely porous beryllium network, and finally (5) sintering the beryllium to obtain a strong, ultra-low-density structure.

Work was done on each step of the process to assess within the limited time available the overall feasibility of the fabrication concept. Major effort was devoted on those steps which provided the maximum difficulty to successful accomplishment or blocked the route to evaluation of subsequent steps. The following tabulation summarizes the steps and delineates the various investigations carried out.

- Fabrication of Near-Spherical Particles

- Ammonium Chloride

- Growth of crystals from saturated and super-saturated solutions

- Fusing and crushing

- Vaporization and condensation

- Pelletizing

- Abrasive rounding

- Condensation buildup

- Naphthalene

- Pressing and crushing

- Fusion and droplet formation

- Gelling of droplets

- Abrasive rounding

- Coating with Beryllium Powder

Dry roll blending

Roll blending with spray addition of wax binder

- Evaporation of Filler Materials

Ammonium Chloride

Vacuum treatments to 143 C

Naphthalene

Vacuum treatments to 88 C

- Isostatic Consolidation

Pressures of 40 and 60 ksi

- Sintering

Vacuum sintering in closed container at 1177 C
and 1260 C

The fabrication of near-spherical particles of the pore forming materials required the maximum effort among all of the processing steps. After many trials involving a wide range of techniques, naphthalene was successfully shaped into near-spherical particles of the desired size range. This was accomplished by dropping of molten beads of naphthalene into liquid nitrogen. The best ammonium chloride particles were obtained by pressing the starting powder followed by crushing and rounding of the edges of the resulting rough, block-like particles. Other techniques for preparing ammonium chloride particles were shown to have promise but could not be exploited because of time constraints.

The pore-forming particles were coated with beryllium powder by rolling the particles in a measured amount of beryllium in a pelletizer. Variations on the basic technique were evaluated; use of a paraffin wax binder in a solvent carrier produced satisfactory results. The resulting powder coating was sufficiently adherent and coherent to withstand operations such as tumbling and pouring.

Coated particles of both pore-forming materials were successfully cold consolidated at isostatic pressures of 40 and 60 ksi without any evidence of specimen fracture.

Evacuation treatments were performed in vacuum at temperatures which effectively removed the evaporable filler materials during an overnight period. The temperatures found effective in removing ammonium chloride and naphthalene were 143 and 88 C, respectively. Removal of the pore former was effected without damage to the frail network of pressed beryllium.

The "green-pressed" beryllium structures, evacuated of filler material, were sintered under vacuum within a closed container. Sound structures were obtained from a one-half hour sintering treatment of 1177 C. Surface crazing resulted only when the heat-up rate was too rapid.

The final sintered structures were evaluated for density, metallurgical structure, and compressive strength.

CONCLUSIONS

- (1) It is feasible to fabricate beryllium structures with a density of the order of 15 percent of theoretical and 1 mm pores by the technique investigated.
- (2) The crush strength of the feasibility samples was substantially lower than could be expected from an idealized structure of the target density.
- (3) Several process improvements are needed to improve the structure and its strength. The pores should be made more spherical and uniform in size. Web thickness should also be made more uniform and of higher density.
- (4) Specific process areas to be optimized include:
 - (a) Spherodization and sizing of the pore forming particles
 - (b) Minimization and control of the binder addition during powder coating
 - (c) Control of powder coating thickness
 - (d) Complete removal of the binder coincident with evaporation of the pore former
 - (e) Modification of beryllium sintering procedure to improve particle bonding and density.

RECOMMENDATIONS

A program of premanufacturing process development and optimization should be undertaken. Further evaluation of filler-particle spherodization techniques should be done to provide an ideally spherical particle and a maximum yield of particles in a narrow size fraction. The particle coating process should be refined to minimize the amount of binder used. The evaporation and sintering treatments should be studied in greater depth for the purpose of minimizing decomposition of carbonaceous constituents and resulting formation of beryllium carbide in the sintered structure. All of the above should be undertaken in a closely coordinated effort to maximize the strength and uniformity of the final product.

FABRICATION OF ULTRA-LOW DENSITY BERYLLIUM

by

John J. Mueller

BACKGROUND

In applications where structures of light weight and reasonable strength are required, beryllium has commonly been chosen because of its inherently low density, high stiffness, and other attractive properties for specific applications. A need for ultra-light metal structures having bulk densities of the order of 0.25 g/cm^3 with fine, uniformly distributed pores has presented a significant challenge to the materials fabricator. One technical approach to the problem has been successful in yielding beryllium sample structures approaching 10 percent of theoretical density; however, the resulting pores are larger than desired for some applications. The technique used involves the following sequential procedures of fabrication: (1) stacking copper balls into a perfect array which in essence constitutes the array of pores desired in an ultimate structure, (2) filling the interstitial spaces with beryllium powder, (3) consolidating the composite by hot isostatic pressing (HIP) to produce a fully densified beryllium network, (4) leaching out the copper to leave a beryllium skeleton, and finally (5) etching away the surfaces of the skeleton to reduce the overall mass and the bulk density of the structure to the desired level.

This approach has been successful with copper balls generally no smaller in diameter than about 0.1 in. As the ball diameter is decreased, one encounters critical problems associated with both powder loading and leaching out of the copper balls. In the case of powder loading, the finer channels between the smaller balls restrict the free flow and uniform packing of the beryllium powder particles. Changing to finer powder particles to aid in the ease of filling into the channels decreases one's ability to achieve an adequate and uniform pack density as a result of the "fluffy" nature of

very fine powder. Assuming that a well-filled structure is achieved, one now faces the problem of extracting the copper out through channels also decreased in size in accord with the decreased size of the ball. The leaching paths become more torturous. Further, the openings between copper filled cells are smaller and significantly restrict the flow of fresh leaching solution, depleted solution, and the gas generated by the chemical reaction.

The technique involving the use of copper balls appears to be limited to making structures with pores greater than 0.1 in. diameter.

OBJECTIVE

The objective of this experimental program was to determine the feasibility of a selected basic fabrication approach for producing a uniformly porous beryllium structure. The bulk density of the structure should be 15 percent of theoretical and the pores nominally 1 mm in diameter. The effort was directed to exploring the potential of alternative materials and methods of processing associated with the basic concept.

A basic aim in the experimental program was to evaluate the feasibility and limitations of each critical step in the processing sequence. Emphasis was placed on those steps presenting the greatest difficulty.

SELECTED FABRICATION APPROACH

A powder metallurgy approach was used in which pores of known size are formed by second phase particles (filler). The filler particles are evaporated from the structure prior to sintering. Naphthalene and ammonium chloride (NH_4Cl) were chosen as the filler materials to be evaluated. In the process, particles of near-spherical shape are coated with beryllium powder and then consolidated into a solid form by cold isostatic pressing (CIP). A low-temperature thermal treatment in vacuum slowly evacuates the porous

beryllium network of the underlying evaporable filler material. The resulting "green" beryllium structure is then sintered to effect particle bonding and associated strengthening.

Because of the limited time available in the program, BCL and LLL agreed to limit the effort devoted to the development of procedures for making ideally spherical filler particles. Near-equiaxed particles would provide an acceptable form with which to evaluate the feasibility of the overall fabrication concept.

EXPERIMENTAL PROGRAM AND RESULTS

The selected fabrication approach may be broken down into the following discrete steps:

- (1) Fabrication of evaporable filler particles
- (2) Coating of filler particles with beryllium
- (3) Cold consolidation of coated filler particles
- (4) Evaporative removal of filler material
- (5) Sintering of the evacuated beryllium body.

The work performed and the results obtained in association with each of the above steps are discussed separately below.

Fabrication of Evaporable Filler Particles

The two filler materials, ammonium chloride and naphthalene, were obtainable in flake or powder form only. It was necessary to convert the powder into nominally 1 mm, equiaxed particles. The results obtained with each material are discussed individually below.

Ammonium Chloride

Ammonium chloride in fine granular form typically of 99.9 percent purity (reagent grade) was used exclusively throughout the program. A source of coarse granular material of a size suitable for obtaining particles 1 mm

in size was sought, but none was found. As a consequence, it was necessary to convert the powder into larger particles. This was not readily accomplished; therefore, the several methods described below were investigated.

Growth from Supersaturated and Saturated Solutions. A few variations of this approach were tried but found to be unsuccessful. The initial approach involved slowly cooling a supersaturated solution of the salt. Numerous fine, acicular crystals precipitated and settled in a felt-like layer at the bottom of the solution container. A very much slower rate of cooling than was achievable at the time or slow evaporation of the water from a saturated condition might lead to the desired cubic crystal habit. These techniques should be evaluated further in a less time constrained program.

Seeding of a supersaturated solution with a small number of fine, cubic crystals also resulted in general needlelike crystal growth similar to that obtained above. No evidence was seen of the desired uniform growth on the initial seeding stock.

A third variation along this line of investigation involved passing ammonium chloride vapors through a fluidized bed of ammonium chloride particles. The bed was contained in a vertical column which was fluidized by flowing argon into it from the bottom. Ammonium chloride vapors generated by heating the salt to a temperature of about 350 C were fed into the argon stream. Again, only needlelike crystals were formed on the suspended seed particles.

Fusing and Crushing. Two unsuccessful attempts were made to fuse the ammonium chloride in a sealed container to form solid bulk stock. Melting point and vapor pressure data indicate melting to occur at 520 C under a vapor-generated pressure of about 500 psi. In view of the high pressure requirement, the ammonium chloride was sealed in a steel container which was contained in a close-fitting graphite hot pressing die. In the first heating attempt, the ram of the hot press, which restrained the axial plug closures in the die, was forced out of the die from the internal pressure

generated. The can ends were no longer restrained and the container ruptured. In the second attempt, a high initial ram load was applied. The melting temperature was reached, but the internal pressure increased significantly and caused the graphite die to rupture. Evidently the internal pressure generated greatly exceeded the pressure calculated from vapor pressure data.

This approach was discontinued.

Pressing and Crushing. Two variations of this approach were tried. One involved cold isostatic pressing at 100 ksi while the second involved room temperature die pressing at 6 ksi which yielded 86 percent dense material.

The high pressure consolidation treatment yielded a body essentially 100 percent dense. Upon crushing, however, the material reverted to a powder which was as fine as or possibly finer than the initial starting material. The material consolidated at the lower pressure crushed readily into small block-like pieces which could easily be screened into discrete sizes. A sample of these particles in the 12 to 18 mesh particle size range (as-crushed condition) is shown in Figure 1. Each particle consists of numerous small particles bonded together.

The roundness of these particles was improved by rolling them in a container lined with abrasive paper. This product was found acceptable for use in the later processing steps.

Vaporization and Condensation Build Up. Initially, ammonium chloride was evaporated and condensed on a cold surface to form a solid layer which might be broken down into suitable solid particles. The surface of the deposited layer was smooth initially. However, as the coating increased in thickness toward a value of 1 mm, it became irregular with needle-like crystal growth similar to that grown from a saturated water solution.

A supplemental experiment was run in which the ammonium chloride vapors issuing from a heated beaker were allowed to flow up a vertical column

11X

FIGURE 1. 12 X 18 MESH PARTICLES OF AMMONIUM CHLORIDE
PRODUCED BY PRESSING AND CRUSHING

with a temperature gradient along its length. The aim was to determine a temperature where the deposit might build up in a uniform manner to a significant thickness. It was found that the salt deposit formed almost completely along the wall of the beaker with very limited deposition along the vertical column. The material deposited along the wall of the beaker was again rough from needle-like crystal growth. No real difference was seen in the appearance of the coating along the beaker wall despite the gradient that was obviously present along the beaker.

An attempt was made to increase the size and roundness of particles produced by the pressing and crushing technique. In this method, ammonium chloride vapors were carried in heated air into a fluidized vertical column of the coarse particles. The particles had been initially screened through a 30 mesh screen to provide a reference size for growth determination. After a treatment of several hours, the particles were again screened through a 30 mesh screen. A large percentage of the particles would not pass through the screen, giving clear evidence of growth from vapor deposition. The appearance of the particles had changed significantly. The surfaces appeared much smoother, and the bulk particles became nearly transparent as a result of the surface smoothing. A collection of such particles is shown in Figure 2.

This latter method showed considerable promise for making near-spherical particles, but the rate of deposition was quite slow.

Pelletizing. The pelletizing approach involved rotating the crystalline powder in an open-ended drum while wetting it with a solvent. The wetted particles tended to cling together and form small spheres as the clusters of particles tumbled. Relatively uniform spheres were obtained, but the range of sizes produced was too great to be considered practical. The spheres tended to grow rapidly when near 1 mm diameter. Continuous pelletization followed by sintering may be an attractive approach, but the time constraints of this feasibility program precluded such a development.

5X

FIGURE 2. AMMONIUM CHLORIDE PARTICLES AFTER BUILD UP WITH AMMONIUM CHLORIDE VAPORS IN A FLUIDIZED BED

Naphthalene

A reagent grade of naphthalene was chosen for experimental fabrication of equiaxed particles. The as-received material was in the form of flake, too fine for direct use in making large particles. Since naphthalene can be melted at 1 atmosphere and a moderate temperature (approximately 80 C), both fusion and cold processing methods were investigated. Each basic approach is covered separately below.

Pressing and Crushing. Naphthalene flake was readily pressed to near full density at both 6 ksi and 100 ksi, but the resulting billets, when crushed, yielded only irregular fragments or particles. Attempts to round the particles by rolling them in an abrasive-lined container were unsuccessful. The irregular particles tended to bond to one another while standing. This tendency interfered with other potential methods of rounding such as spheroidization in a hot column.

Although far from ideal, a quantity of appropriately sized particles were screened from the crushed material and used to evaluate the coating, pressing, and evaporation characteristics of naphthalene.

Fusion and Droplet Formation. The ease with which naphthalene could be melted provided several approaches to producing near-spherical particles. First, naphthalene was melted in a polyethylene bag and extruded through a hypodermic needle into an ice-cooled bath of water. Nearly spherical particles were obtained, but their size was much in excess of the desired 1 mm diameter. Varied extrusion temperatures and rates continued to yield an unacceptably low yield of small spherical particles.

Dropping molten naphthalene from a pipette into water produced only large cup-shaped splats of the material. The splats were about 20 times the diameter of the droplet released from the pipette. Next, several variations in cooling or chilling of the droplets were evaluated. A crucible with exit holes sized to produce 1 mm diameter droplets was used. Merely dropping the molten droplets through a few feet of ambient air resulted in

splatting of the still-molten droplet. Increasing the drop height to about 8 ft and cooling the air through which the droplet fell resulted in no meaningful improvement. Increasing the drop height to about 40 ft also was ineffective in yielding solid spherical particles.

A satisfactory result was obtained when the molten beads of naphthalene were dropped into liquid nitrogen. This technique provided a high yield of spherical particles in the size range of 8 through 20 mesh, and discrete fractions of 8 x 12 mesh, 12 x 18 mesh, and 18 x 20 mesh were prepared for subsequent fabrication studies. Figure 3 shows a group of typical 18 x 20 mesh particles. The particles are well shaped and near 1 mm. Particles in the 8 x 12 mesh range frequently contained a large, porous depression in the surface. Separation of spherical particles from irregular ones was readily accomplished on a roll separation table.

Particles produced by this method were used extensively in the later experimental work.

Gelling and Solidification of Droplets. Naphthalene was prepared in the form of a gel with water and a soluble organic algenate compound. The gel was dropped from a pipette into a water solution containing a bivalent salt which induced solidification of the gelatinous droplets. Droplets formed in this manner were spherical but generally much larger than desired. When subjected to an evaporation treatment, the spherical particles lost weight but did not decrease in size. After a significant weight loss, only a thin spherical shell remained. The residual shell probably resulted from a concentration of metallic ions at the surface of the spheres. This would clearly lead to contamination of the beryllium if the spheres were used in forming pores. On recognition of this problem, further development of this technique was discontinued. A sample of this type of particle is shown in Figure 4.

18 x 20 mesh

11X

8 x 12 mesh

8X

FIGURE 3. NAPHTHALENE NEAR-SPHERICAL PARTICLES PRODUCED BY DROPPING MOLTEN DROPLETS INTO LIQUID NITROGEN

5.5x

FIGURE 4. NAPHTHALENE PARTICLES SOLIDIFIED FROM A GEL

Coating of Pore-Forming Particles

One basic coating technique, which was varied in several ways, was evaluated and found successful as a method of applying beryllium powder to both types of evaporable pore-forming material. The technique involved roll blending of the evaporable particles with the fine P-1 beryllium powder. Supplemental treatments were performed to improve adherence of the powder coating.

Simple blending of the dry powder with naphthalene particles resulted in an adherent coating of very small thickness. As the thickness increased to a desirable level, localized spalling occurred. No coatings of acceptable thickness were obtained by dry blending. Periodic spraying of the blend with an evaporable solvent aided significantly in producing acceptably thick and apparently uniform coatings on particles of both filler materials. Unfortunately, the resulting coatings were not very durable and were easily damaged when the particles were poured from one container to another. The coating on naphthalene was less adherent than on ammonium chloride because of naphthalene's greater volatility. A two percent addition of paraffin wax in the solvent increased the adherence of the beryllium particles. The coatings made with wax binder additions were very tenacious and could withstand tumbling and pouring. Figure 5 shows the appearance of naphthalene particles coated with beryllium powder.

Three particle size ranges were used in grouping particles for coating purposes and use in subsequent processing steps. The three ranges were selected on the basis of available standard screen sizes. The ranges and their associated dimensions are as follows:

8 x 12 mesh - 2.38 x 1.68 mm

12 x 18 mesh - 1.68 x 1.00 mm

18 x 20 mesh - 1.00 x 0.84 mm.

It is possible to obtain screens which are sized to obtain a much smaller variation in size. The use of such screens was considered impractical for this program, because of the small yield of particles in a yet narrower size fraction.

12 x 18 mesh

5X

8 x 12 mesh

11x

FIGURE 5. NAPHTHALENE PARTICLES COATED WITH BERYLLIUM BY ROLL
(A wax fugitive binder was used to enhance coating adherence)

Once an acceptable coating method was established, the procedure was modified so as to yield control of the thickness of the coating and distribution of the beryllium among the coated particles. To accomplish this, discrete particle fractions of the filler material were used. For each size fraction, the required weight of beryllium powder needed was calculated as a function of filler particle size and weight of charge in the blender. The beryllium powder was added in small batches until all was consumed in forming coatings.

Cold Isostatic Pressing (CIP) of Coated Particles

Two CIP pressures, 40 and 60 ksi, were used in making trial pressings of coated particles of both filler materials. Two pressures were used because of an anticipated problem of springback of the low-modulus filler materials which could fracture the beryllium network. The higher pressure (60 ksi) is commonly used in cold consolidation of beryllium for HIP processing. The "green" body produced at this pressure was strong and durable. The lower pressure (40 ksi) is the lowest value which will yield a sound but fragile body.

The first trial pressings were made on coated ammonium chloride particles. Both pressures yielded visually acceptable bodies with no external evidence of fracture. Figure 6 shows a representative as-pressed pellet. It is interesting to note that the relatively thin outermost coating over the particles remained intact and was not broken away as a result of adherence to the mold material. The molds were of polyurethane with cavities of about 1 in. diameter by 1-1/2 in. long. The resulting pellets were nominally 3/4 in. diameter by 1 in. long.

The results obtained in pressing the coated naphthalene filler particles did not differ from those obtained from ammonium chloride. No springback problem was observed irrespective of filler material, filler particle size, or amount of beryllium.

~2-1/2X

~2-1/2X

FIGURE 6. COLD ISOSTATICALLY PRESSED PELLET OF BERYLLIUM-COATED AMMONIUM CHLORIDE 18 X 20 MESH PARTICLES

Evaporation of Filler Materials

The first evaporation trials were made with ammonium chloride filler because of its earlier availability in coated form. A preliminary evaluation of the evaporability of ammonium chloride was made on a pellet of coated irregularly shaped particles which were simply die pressed to shape at a pressure of 30 ksi. The pellet was slowly heated to a temperature of 300 C under vacuum in a gravimetric balance during an overnight period. The ammonium chloride was completely removed, leaving a sound, 46.5 percent dense structure. There was no evidence of damage to the beryllium from the treatment, and the beryllium structure was quite durable. Figure 7 compares the evaporatively-treated, die-pressed pellet with one in the as-pressed condition. The experiment indicated that ammonium chloride could be successfully removed at 143 C (300 F).

The first trial evaporation treatment made on an isostatically pressed pellet was made at 143 C (300 F) for a period of 6 hours. It was found during a subsequent sintering trial that not all of the ammonium chloride had been removed. The pellet burst during sintering as a result of internal pressure developed at elevated temperature. The failed pellet is shown in Figure 8.

Subsequent evaporation treatments were made at 143 C (300 F) for an overnight period of nominally 18 hours. This was effective in removing all of the ammonium chloride from the size of pellet being used.

Some evidence was found in later sintering treatments that the paraffin binder was not being removed effectively by the 143 C (300 F) treatment. This necessitated the addition of a subsequent treatment at 260 C (500 F) for about 4 hours to remove the residual wax. Evidence was found in later sintering experiments that a still higher evaporation temperature is required to remove all of the wax.

The greater volatility of naphthalene prompted the initial evaporation trials with this material to be done at room temperature. Only a slight amount was lost during the period of a work day. With the temperature

2X

FIGURE 7. DIE-PRESSED AMMONIUM CHLORIDE CONTAINING PELLETS: ONE EVAPORATIVELY TREATED (LEFT) AND ONE IN THE AS-PRESSED CONDITION (RIGHT)

3X

FIGURE 8. PELLET WHICH BURST DURING SINTERING AS A RESULT
OF RESIDUAL AMMONIUM CHLORIDE

increased to only 32 C (90 F), an overnight period was effective in evacuating all of the naphthalene. The specimen used in this determination was made without wax binder in the coating solvent. Therefore, the pellet was approximately 10 percent dense because of incomplete coating buildup. The pellet remained intact but was easily damaged during handling.

Subsequent naphthalene-containing pellets were made with wax added to the solvent used in the coating operation which increased beryllium content. Pellets containing wax binder could not be effectively evacuated of naphthalene at 32 C (90 F). The evaporation temperature was increased to 88 C (190 F) which was effective and caused no damage to the beryllium structure.

Figure 9 shows the typical appearance of a pellet evacuated of naphthalene. It shows localized breakout of some of the peripheral walls which also occurred during evacuation of ammonium chloride.

Sintering

Sintering of the porous beryllium pellets was done in a vacuum furnace with the pellets held in a steel container. The container consisted of a cup member which was covered by a second inverted cup of slightly larger diameter. This arrangement was chosen to minimize the loss of beryllium by evaporation and to thereby maintain an atmosphere of beryllium around the pellet to aid in sintering. In earlier work at BCL, it was shown that a sealed container around porous beryllium bodies enhanced the formation of rounded pore surfaces which improved the ductility of the sintered product. This exact approach could not be instituted in this work because of the delicate nature of the "green" bodies being sintered. The handling involved in welding and subsequently opening the container following sintering were considered excessive for the delicate product being produced.

The steel container was lined with tantalum to provide a compatible high temperature material and to getter oxygen released by the pellet during heat up. A temperature of 1177 C (2150 F), which is 100 F higher than used in earlier work, was used in sintering most of the specimens prepared. The

FIGURE 9. EVAPORATIVELY TREATED PELLET MADE WITH NAPHTHALENE FILLER PARTICLES OF NEAR-SPHERICAL SHAPE

higher temperature was chosen to enhance sintering of these structures, since they could not be expected to be as effectively cold consolidated with paraffin wax being used as binder material.

The first pellet subjected to the sintering treatment was found to be structurally strong but contained a number of surface cracks which were considered to be the result of too rapid a rate of temperature rise. Figure 10 shows the types of cracks encountered. Subsequent specimens were heated at the normal rate to 871 C (1600 F) and then at a reduced rate to 1177 C (2150 F). Typical times to 871 C (1600 F) and from that temperature to 1177 C (2150 F) were 0.8 - 1 hour and 1.75 - 2 hours, respectively.

The pellets sintered under these conditions were sound with no apparent structural defects. Figure 11 shows the exposed internal cell structure of an early specimen made with irregularly shaped filler particles. The structure of the sintered webs is shown in Figure 12. As can be seen, the beryllium particles are joined only at random points but bonded sufficiently to produce a continuous and interlocking network of particles. The webs are of varying thickness which could be expected to cause the strength of the composite to be controlled to a large extent by the locally occurring thin sections.

In one case, the sintering temperature was increased to 1260 C (2300 F) to determine its potential in effecting greater web densification. A tungsten-lined graphite sintering container was used for compatibility at this temperature. The container was not tight and about half of beryllium pellet was lost as vapor during sintering. No further work was done at this temperature.

To verify the adequacy of the 1177 C (2150 F) sintering treatment, a pellet similar in size to the high porosity pellets was prepared from P-1 beryllium powder only. The pellet was cold consolidated at 60 ksi which yielded a density of 78.4 percent. Sintering increased the density to 89.2 percent. This was considered quite acceptable for such a notably poor sintering material.

FIGURE 10. SINTERED PELLET WITH SURFACE CRACKS FROM EXCESSIVE RATE OF TEMPERATURE RISE

FIGURE 11. VIEW OF INTERNAL CELL STRUCTURE OF PELLET MADE WITH IRREGULARLY SHAPED AMMONIUM CHLORIDE PARTICLES

100X

500X

FIGURE 12. SINTERED WEBS OF PELLET (NO. 4-4) MADE WITH IRREGULARLY SHAPED AMMONIUM CHLORIDE FILLER PARTICLES

The majority of the experimental porous pellets were found to generally decrease in overall dimensions by an amount ranging between 8 and 12 percent. It should be noted, however, that it was not possible to obtain accurate dimensional measurements on the pellets. The pellets were measured in their as-evaporated and as-sintered conditions in which the rough surfaces and rounded corners contributed to error. Some surface material which was lost during handling also contributed to lower accuracy.

In one case, two trial pellets were sintered simultaneously. Neither pellet changed dimensionally. There was no possible explanation for this, since the temperature cycle and vacuum conditions appeared normal and did not differ from other sintering runs.

In the early trials, the weight loss from sintering was as much as 0.4 to 0.5 g. Since the pellets contain only about 1.5 g of beryllium, the weight loss was unreasonable. The loss was attributed to wax which was not removed during evaporation treatments performed at 143 C (300 F) and lower. The pellets smelled of acetylene and methane which indicated the presence of reaction products from beryllium carbide contacting water vapor in the air. The carbide was evidently formed by reaction with the residual wax during rapid heating in the sintering treatment. The weight loss and evolution of hydrocarbon gas was found common to pellets made with either ammonium chloride or naphthalene filler material.

A 260 C (500 F) heat treatment following the basic evaporation treatment decreased but did not eliminate the weight loss during sintering. Limited time did not permit evaluation of higher evaporation temperatures.

The furnace atmosphere during sintering of the low-density pellet was generally no better than about 5×10^{-4} torr. This was apparently the result of continuous gas evolution from residual binder and decomposition products in the pellets. In contrast to this, it was found that the furnace atmosphere was in the 10^{-5} torr range when the trial P-1 beryllium pellet was sintered. This pellet contained about six times the amount of beryllium and did not contain a filler material or binder.

Evaluation of Sintered Structures

The microstructure, density, and crush strength of several sintered samples were determined. Crush strength was determined on pellets in the as-sintered condition. Machining of the pellets to obtain perfect right circular cylinders was avoided because no proven machining technique existed and consequently the risk of losing the small number of specimens available was unacceptable. To avoid stress concentrations, the ends of the pellets to be contacted by the load platens were cushioned with two sheets of a fibrous blotter paper. During load application, the buffer layer assumed the contour of the end of the pellet, thereby minimizing localized crushing of the web structure. This layer also minimized effects of nonparallelism of the end faces. The results obtained, therefore, are considered reasonable approximations of the true crush strengths of the pellets.

The load was applied at a rate of 0.01 in./min and the resulting load versus time curve was used to obtain the ultimate crush strength and an estimate of the stress at initial yielding. The point of yielding was taken as that point at which the load curve became nonlinear.

Table 1 summarizes the results of density and strength determinations made on nine experimental pellets produced with: (1) varied sizes of pore formers, (2) both types of pore-forming materials, and (3) varied beryllium particle size.

Density varied from a low value of 10.3 to a high of 24.7 percent of theoretical. The indicated values are probably somewhat lower than actual because the dimensions were measured on as-fabricated pellets. The rounded corners and dimpled surface would cause the actual volume of the pellets to be lower than calculated.

Pellets 45-1 and 45-2 did not experience a volume change during sintering. However, their strength values are similar to other pellets prepared from 10 μ m powder. The strength values of the -325 mesh specimens are inappropriately low for their comparatively high densities. The structure of the stronger of these two specimens is represented by the micrograph of Specimen No. 4-4 which was shown earlier in Figure 12.

TABLE 1. SUMMARY OF DATA ON COMPRESSIVE STRENGTH AND DENSITIES OF SINTERED PROCESS PELLETS

Specimen No.	Filler Particles		Be Powder Size	Percent Theoretical Density ^(b)	Compressive Strength, psi	
	Type	Mesh Size			Yield ^(c)	Ultimate
4-3	A	12 x 18	-325 mesh	24.7	1200	1530
41-3	N	8 x 12	-325 mesh	17.9	181	199
45-1	N	8 x 12	-10 μm	10.3	753	784
45-2	N	8 x 12	-10 μm	11.9	1279	1377
45-3	N	+8	-10 μm	17.2	948	994
47-1	N	12 x 18	-10 μm	14.2	1196	1448
47-2	N	12 x 18	-10 μm	17.7	663	916
49-2	N	12 x 18	-10 μm	15.1	1102	1182

(a) A, ammonium chloride; N, naphthalene.

(b) Value based on weight and volumetric measurement.

(c) Point of deviation from straight-line loading behavior.

The cause of the very low strength value of Specimen 41-3 can be recognized from metallographic examination of a sister pellet (41-4) which was made from the same batch of coated naphthalene particles. Typical webs of Specimen 41-4 are shown in Figure 13. One can clearly see two basic causes of weakness of the specimen. First is the division of the webs by lines of unbond. Second is the relatively high degree of separation of the individual particles from one another (see Figure 12 for comparison). The structural deficiencies of the No. 41 lot of specimens are believed to be caused by excessive wax binder application during the coating process. The wax apparently prevented effective contact between individual beryllium particles during subsequent consolidation of the coated particles.

The comparatively low strengths of the specimens made from minus 325 mesh P-1 beryllium powder were believed additionally to have been greatly affected by the small number of particles that can exist across a web section.

Therefore, subsequent specimens were prepared from minus 10 μ m powder. Figure 14 shows the microstructure of webs in such a specimen.

DISCUSSION

Pore-forming particles, both ammonium chloride and naphthalene, suitable for evaluation were successfully produced on an experimental basis. Ammonium chloride particles were prepared by pressing powder, crushing the pressed billet into agglomerate particles, and rounding the irregular edges by roll blending in a drum lined with abrasive material. The resulting particles were nearly equiaxed with undulating surfaces.

Further effort would be required to obtain particles of ammonium chloride of improved shape. Vapor deposition of ammonium chloride onto a fluidized bed of particles appears promising for improving the shape of rounded agglomerate particles, but this approach is not expected to yield a near-spherical product. An approach whereby solid particles can be tumbled over a hot surface or passed through a gas flame or gas plasma could be evaluated for rounding of the particles to near spherical shape. Also,

100X

100X

FIGURE 13. TYPICAL DEFICIENCIES CAUSED BY EXCESS WAX BINDER
Specimen was prepared from -325 mesh powder and
exhibited very low strength

100X

250X

FIGURE 14. TYPICAL WEB MICROSTRUCTURE OF SPECIMEN
PREPARED FROM $-10\mu\text{m}$ BERYLLIUM POWDER

mechanical methods of rounding such as are used in grinding small ball bearings might yield an acceptable product. These alternatives could not be evaluated because of our inability to produce fully dense starting particles.

The best naphthalene particles were made by dropping molten droplets into liquid nitrogen. The resulting particles were nearly spherical. The larger particles frequently contained surface cavities, but the presence of surface cavities in the particles of desirable size was relatively infrequent.

Coating of the pore-forming particles with beryllium by blending of the mixture and simultaneously spraying with a solvent containing a paraffin binder appears to be an acceptable method. Refinement of the coating technique is required, however. The amount of paraffin binder required must be controlled and minimized. Excessive paraffin hinders both compaction and sintering. Therefore, strength of the sintered product is adversely affected. The volume of binder cannot exceed the volume of pore space in the cold pressed beryllium body. The presence of carbides in the sintered product is believed to stem from decomposed residual wax. It may be necessary to heat up at a slower rate and to a higher temperature during the evaporation cycle to assure complete removal and avoidance of decomposition of the wax. It is conceivable that the torturous path traveled by the evaporating molecules causes fairly high internal pressure when the temperature is increased too rapidly. Such a condition favors decomposition of paraffin.

Further research may identify a substitute for paraffin which might minimize or avoid the problem of decomposition and subsequent carbide formation.

The coating procedure used in the present research assured a fixed filler particle/beryllium powder ratio by weight but did not control wax binder weight nor assure uniform distribution of the binder. The results of this investigation indicate that the binder concentration increased as a function of coating thickness and that the total volume of binder exceeded the available pore volume of the beryllium coating after CIP (about 20 percent). As a consequence, the webs (coating) did not compact to the degree expected, gaps were left at the web center line (coating interfaces), sintering could not

proceed in normal fashion, and crush strength was below expectation. A coating procedure which controls the filler particle/beryllium powder ratio and the binder/beryllium powder ratio is needed. This could be accomplished on a volumetric (particle diameter) basis if the filler particles were made more spherical and uniform in diameter. It should then be practical to roll the filler particles in an excess volume of beryllium powder. An arrangement would be needed to meter the application rate of the binder spray which must be of known concentration. Hence, the total volume of wax could be controlled. Periodically, the coated particles would be screened and undersize particles returned to the coating drum.

Since no problems were encountered in isostatic pressing of any of the experimental pellets, it appears that pressing at 60 ksi in polyurethane molds is a satisfactory procedure. The 60 ksi level is also compatible with the capabilities of available large autoclaves.

Sintering at 1177 C (2150 F) in vacuum in a nearly-closed vessel appeared to yield a satisfactory degree of dimensional change in the pellets.

CONCLUSIONS

- (1) The fabrication approach whereby equiaxed particles of ammonium chloride or naphthalene are used to form internal pores in beryllium by being
 - (1) coated with beryllium powder, (2) isostatically consolidated, and (3) removed by evaporation prior to final sintering is feasible for producing beryllium structures with a density of the order of 15 percent of theoretical and one mm pores.
- (2) The following specific areas in the process require additional effort:
 - (a) Develop an improved method of producing spherical particles of ammonium chloride and/or optimization of the procedure for making naphthalene spherical particles.
 - (b) Establish an optimum evaporation schedule which will eliminate or minimize the decomposition of the wax binder and assure its complete removal or evolve an acceptable substitute for the wax.

- (c) Establish an optimum filler-material size fraction and associated coating and separation procedure which will yield optimally coated particles with a prescribed ratio of beryllium to filler material.
- (d) Optimize the various fabrication steps to obtain porous structures of maximum strength.

NOTICE

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