THE PRODUCTION OF HIGH-PURITY BERYLLIUM CARBIDE

by

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Cleveland, Ohio

Contract AT-(30-1)-541

Issued October 15, 1952

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ABSTRACT

A commercial method for the preparation of very pure beryllium carbide in quantities up to 140 pounds per run is described herein.

This process, utilizing the reaction between −200 mesh beryllium powder and −325 mesh ink-grade graphite powder is carried out preferably in graphite dies under small mechanical pressures at a temperature in the neighborhood of 1000°C.

The effect of variables such as stoichiometry, temperature of reaction, beryllium powder particle size and materials of construction are discussed.

A. PURPOSE

The production of high-purity beryllium carbide was undertaken because of the potential use of this material as a high-capacity moderator. During the past several years, the NEPA project, then operated by the Fairchild Engine and Aircraft Corporation, was interested in obtaining very pure beryllium carbide in order to test its applicability to air-borne nuclear reactors. The principal impurity present in the available grades of beryllium carbide which was considered extremely detrimental was nitrogen.

The purpose of this project was not only to prepare very pure beryllium carbide for test purposes, but also to develop a process for the production of beryllium carbide on a commercial scale while retaining the degree of purity attained in the laboratory. It was also of considerable importance to determine the most economic method of preparing a technically acceptable product.

B. INTRODUCTION

Historically, the original preparation of beryllium carbide appears to have been carried out by Lebeau in 1895 (reference 1). Lebeau prepared the compound, Be_2C, by two methods, namely, the reaction between beryllium metal and sugar charcoal and the reduction of beryllium oxide with sugar charcoal. He was able to prepare a sufficient quantity of the carbide to measure its chemical reactivity with a variety of reagents.

The recent work on the preparation of beryllium carbide has been centered in the efforts of the NEPA project (GE-ANP after June, 1951) and its subcontractors. A summary of the various methods of preparation is among the publications of that group and will not be repeated here (reference 2).

However, it is of interest to describe the commercial process which was heretofore used by the Fansteel Metallurgical Corporation to produce the only commercially available beryllium carbide. This process used the second method of Lebeau for which the equation is:

$$2BeO + 3C \rightarrow Be_2C + 2CO$$

Refractory grade beryllium oxide was blended with commercial lamp-black in stoichiometric quantities with about 1.5% by weight excess carbon. The charge was then heated in a graphite crucible to the temperature range 2050-2100°C. with an induction coil. The product was described as being composed of friable red crystals of beryllium carbide containing very hard lumps of apparently fused carbide. The product yield was about 71% or 1.2 pounds. Table I gives the analysis of this product as given in reference 2. It is of interest to note that according to reference 2, the quality of the beryllium carbide dropped considerably when production was increased by multiple firing of charges.

Table I—Chemical Analyses of Commercially Available Beryllium Carbide

	Lot No. 8	Lot No. 15
Total Be	58.06%	58.81%
BeO	1.88	1.13
Be_3Na	2.90	2.94
$BeO \cdot H_2O$	0.00	0.10
Moisture	0.00	0.06
Free Carbon	1.74	0.96
Be_2C	92.95	94.82
SiO_2	0.14	0.05
Total	99.61	100.06

Note: This material was supplied by Fansteel Metallurgical Corporation to NEPA in 1950. This analysis is taken from reference 2.

The first reaction for the production of beryllium carbide investigated by the Brush Beryllium Company was the sodium reduction of beryllium fluoride in the presence of carbon according to the following reaction:

$$6BeF_2 + 4Na + C \rightarrow Be_2C + 4NaF \cdot BeF_2$$

The reaction was carried out by blending stoichiometric amounts of the reactants and heating them to 1000°C. in a graphite crucible. The reaction took place exothermically and gave a product containing about 50% Be_2C. Purification from the sodium fluoberyllate by-product was attempted by vacuum sublimation, but the fluoberyllate apparently decomposed into its component sodium and beryllium fluorides before sublimation and allowed the sodium fluoride to bring about a 25% reaction reversal. Attempts were also made to remove the excess carbon present by preferential air elutriation and oxidation, but neither of these methods were successful. It was found that the entire sample oxidized rapidly when treated at 500°C. under an oxidizing atmosphere.

The production of beryllium carbide by the reduction of beryllium oxide with carbon in a process similar to that used by Fansteel was attempted. After several trials which produced a poor quality of carbide containing a high percentage of beryllium nitride, as was the case in the Fansteel product, this method was also abandoned. As the nitrogen pick-up occurred both under a vacuum and an inert gas atmosphere, it was presumed that the nitrogen was adsorbed on the graphite crucible. Even with a high quality product this reaction would not have been too attractive because of the difficulty in attaining and maintaining a high production rate.

The work was then directed towards the production of beryllium carbide by means of a reaction between beryllium and carbon powders. It was found that this reaction proceeded at about 1000°C., a much lower temperature than the beryllium oxide-carbon reaction. At this lower temperature the rate of reaction of nitrogen with the charge is so low that only about 0.05% or less nitrogen is contained in the product. Thus the beryllium metal-carbon reaction carried out with large reacting surface areas is basically a superior process to the beryllium oxide-carbon reaction, which produces a product containing 2 to 3% Be_3N_2, even if the latter reaction can be driven to 100% completion. The bulk of the work on this project as reported below dealt with the development of a commercially attractive process for the production of beryllium carbide utilizing this reaction.

C. EXPERIMENTAL WORK

1. Initial Investigations

The first experiment for the production of beryllium carbide from beryllium powder and carbon utilized stoichiometric amounts of beryllium and activated carbon according to the following equation:

$$2Be + C \rightarrow Be_2C$$

The materials were blended, heated to about 1100-1150°C. and held at this temperature for 24 hours under an atmosphere of helium. While the beryllium carbide content of the product was only about 75%, the ash content of the activated carbon used for this run was 23.0% which explained the rather low product yield.

Acheson ink grade graphite (99.8% C) was substituted for activated carbon in the second run using the beryllium powder-graphite reaction. The stoichiometric quantities of −200 mesh beryllium powder and −325 mesh graphite were heated in a graphite crucible. The reaction was found to take place exothermically at about 910°C. by means of a nickel thermocouple well embedded in the one pound charge. The heat of reaction was sufficient to melt the nickel thermocouple tube allowing the helium atmosphere to be replaced with air. Despite this exposure at elevated temperature, the product analyzed 95.8% beryllium carbide with 2.74% BeO, 0.052% Be_3N_2 and 0.91% free carbon.

With the discovery that a relatively pure beryllium carbide could be produced at low temperature by the direct combination of beryllium and carbon powder a number of small runs using one and four pound charges were made to furnish material for testing by the ANP project. During the production of this material the trend of investigation was aimed at improving the quality of the beryllium carbide product. The specifications as to the chemical analysis of acceptable beryllium carbide established by the ANP group is shown in Table II.

2. Effect of Stoichiometry Upon the Purity of Beryllium Carbide

The beryllium carbide produced by the reaction between −200 mesh beryllium powder and −325 mesh ink grade graphite is a light brown semi-sintered mass which can be easily ground to −200 mesh or below in a ball mill.

The major impurities encountered with this method are beryllium oxide, free carbon, moisture and the metallic impurities present in the beryllium metal originally. The powder state of this beryllium carbide precluded the use of any leaching techniques in purification as the material was quite hygroscopic and easily oxidized. Thus, a technique for removing free beryllium metal from beryllium carbide with dilute hydrochloric acid which has been suggested (reference 3) would have been impractical. Similarily, efforts to reduce the free carbon content of the product by treatment after reaction failed. Upon heating a sample to 500°C. under an oxidizing atmosphere in an attempt to burn off the carbon, the entire sample oxidized rapidly. Air elutriation experiments were not successful in obtaining a fractionation of the free carbon content.

The product is recovered with a thin grayish film on all surfaces of the charge when the reaction is carried out in graphite. Removal of this layer is easily accomplished, but on one pound charges, the scrapings amount to about 4% of the product. These scrapings contain a considerable amount of beryllium oxide and free carbon as compared to the rest of the product as shown in Table III.

Table II—Specifications Established by ANP for Maximum Impurity Limits in Beryllium Carbide

Nitrogen	0.1 max. %
BeO	1.5
Free Carbon	1.0
Moisture Evolution at 700°C.	0.2
Other Impurities	The sum total of all other impurities in the product shall not exceed 0.3% by weight. No other single impurity shall exceed 0.2% by weight.

Table III—Analysis of Surface Scrapings and Remainder of Product From One Pound Beryllium Carbide Run

	Scrapings	Grab Sample	(ground) Remaining Product
BeO	6.36%	1.30%	1.64%
Be_3N_2	0.033	0.021	0.02
Free C	9.63	0.38	0.49
H_2O	0.86	0.26	0.19
Be Assay	57.17	59.58	59.87
% of Total Charge	4.1	2.0	93.6

An investigation was made of the possibility of lowering the beryllium oxide content of the entire charge, as well as that of the surface layers, through the addition of small amounts of excess carbon. It was hoped that this addition would bring about the reaction:

$$2BeO + 3C \rightarrow 2CO + Be_2C$$

However, as can be seen by the data in Table IV, additions of 5 and 20% excess carbon failed to bring about this reaction at the maximum temperatures of 1200°C. involved in the runs. The reaction was monitored by the relative free carbon content as this was a more precise determination than the oxide analysis. The desired side reaction would have resulted in pronounced negative values in remainder column. In the case of the 20% excess carbon run, the negative value is within the analytical error and was not interrpreted as a meaningful value.

As beryllium oxide was the largest impurity present in the products of one and four pound charges, it was concluded that the best possible ratio of reactants in the beryllium metal-graphite reaction is the exact stoichiometric ratio with an allowance made for the amount of beryllium oxide present in the starting beryllium powder.

Table IV—Effect of Excess Carbon Additions on the Beryllium Powder-Graphite Powder Reaction

Charge	Calc. Excess on Total Charge	Free Carbon Analysis	Remainder
Stoichiometric	-----	1.91%	-----
5% Excess C	1.96%	4.85	+0.98%
20% Excess C	7.41	9.22	−0.10

Remainder = (Free Carbon Analysis) − (Control free carbon + Calculated Total free carbon)

3. Investigation of the Effect of Beryllium Powder Particle Size

The reaction between beryllium and graphite proceeds very rapidly with the evolution of considerable heat when both reactants are in the finely divided state. The reaction between −200 mesh beryllium powder and −325 mesh graphite proceeds at a temperature of about 910° as has been described above.

As the beryllium powder particle size decreases with a corresponding increase in surface area, the beryllium oxide content of the powder also increases. Thus, it was of interest from a technical viewpoint to investigate the reaction using coarser beryllium powder than the −200 mesh material. Also from an economic standpoint, a saving would be made by reducing the required number of passes through the attrition mill when using coarse powder.

The screen analyses of the powders used in this investigation are shown in Table V. The reaction data obtained are shown as Table VI.

Table V—Screen Analysis of the Various Beryllium Powders Used in Producing Beryllium Carbide

Sieve Fractions	1st pass* powder	2nd pass −60 mesh	2nd pass −60 + 400 mesh	4th pass −100 + 400 mesh	4th pass −100 mesh	−200 mesh
+ 20 mesh	0.71%	---	---	---	---	---
− 20 + 30	1.05	---	---	---	---	---
− 30 + 40	10.87	---	---	---	---	---
− 40 + 60	36.78	---	---	---	---	---
− 60 + 100	25.82	40.03%	45.65%	---	---	---
−100 + 150	9.02	19.47	22.19	33.95%	22.32%	0.17%
−150 + 200	4.04	11.41	13.05	22.93	15.09	1.27
−200 + 250	1.68	5.76	6.57	12.92	8.50	0.68
−250 + 325	1.84	6.10	6.95	15.67	10.30	21.71
−325 + 400	1.37	4.26	4.96	14.37	9.45	18.45
−400	5.94	12.26	---	---	34.14	57.57

*Pass refers to the number of times the material has passed through the attrition mill.

Examination of this data reveals a definite temperature of reaction-beryllium particle size relation. The temperature at which there occurred a sharp increase in the heating rate, as measured on the outside of the crucible, was taken as a satisfactory reaction temperature for comparison purposes.

The standard procedure which was established with the −200 mesh beryllium powder consisted of heating the charge to the point where the exothermic reaction begins as indicated by temperature

Table VI—Data on Beryllium Carbide Runs Using Varying Beryllium Powder Particle Size

Run No.	Beryllium Pow. Description	BeO Content of Be Powder	Crucible Material	Reaction Temp.*	Product		% Reaction
					BeO	Free C	
12	1st Pass**	0.39%	Graphite	1100°C	3.43%	3.28%	91.4%
24	−60 + 400 mesh 2nd pass	0.72	Iron	1090	---	18.45	53.3
24	−60 + 400 mesh 2nd pass	0.72	Nickel	1090	---	20.45	48.9
25	−60 mesh 2nd pass	0.69	Nickel	1075	---	21.75	45.3
28	−60 mesh 2nd pass	0.69	Graphite	1050	1.35	0.68	97.6
27	−100 + 400 mesh 4th pass	0.50	Graphite	1013	1.01	0.33	98.7
29	−100 mesh 4th pass	0.69	Graphite	1002	0.45	0.24	98.7
Av. of 5 runs	−200 mesh	1.21	Graphite	938	1.03	0.63	97.2

*Temperature is measured on outside of reactor in all cases.

**Pass refers to the number of times the material has passed through the attrition mill.

measurements on the outside of the reactor. The furnace power was then stopped and the charge allowed to cool, the exothermic heat being great enough to essentially complete the reaction. However, from Table VI, it is apparent that this is not the case for coarser powders as runs 12, 24, and 25 were run in this manner. Working on the hypothesis that the fines present in the coarser powders were reacting at a much lower temperature than the coarser material without liberating enough heat to react the larger particles, runs 27, 28, and 29 were heated beyond the indicated reaction point to about 1200°C. In the case of run 29, two reaction points were observed on the time-temperature curve, the first occurring at 1002° and the other at about 1110°C.

It therefore appears that beryllium powder coarser than −200 mesh may be used for the production of beryllium carbide if allowance is made for the necessary increase in temperature to bring about the second portion of the reaction.

4. Materials of Construction for Producing Beryllium Carbide

A thorough investigation of the possible crucible materials for the production of beryllium carbide has not been conducted due to the fact that satisfactory results were obtained using graphite crucibles.

The beryllium oxide level in four pound beryllium carbide lots produced in graphite has repeatedly been in the range of 1.3-1.4% with a starting BeO content in the beryllium powder of about 0.7%. The crucibles in use with these charges allowed 53.5 square inches of the charge surface to contact the graphites per pound of charge. When the reaction was carried out in 1½" I.D. by 2" high graphite crucibles with a contact surface of 181.5 in.²/lb. of charge, the oxide analysis increased to 2.50%. This, coupled with the previously mentioned presence of a skin on the beryllium carbide product which is high in beryllium oxide and consequently high in free carbon, has led to the hypothesis that a reaction poisoning occurs in graphite due to the presence of the clay (Al_2O_3) binder used in graphite fabrication.

While this poisoning has not been of such serious nature as to bring the purity of the beryllium carbide below the specifications shown in Table II, it was deemed advisable to investigate methods of eliminating

this phenomena. One four pound run was made in a graphite crucible lined with molybdenum sheet to check the above hypothesis as to the source of the oxide pick-up. The starting BeO content of the beryllium powder was 0.72%. The product analyzed 0.80% BeO, a material lowering of the oxide pick-up illustrating the value of lining graphite crucibles.

Other linear materials, such as iron and nickel have been considered, but were by-passed in favor of molybdenum because of their relatively low melting points.

5. Large Scale Production of Beryllium Carbide

Three pilot plant scale beryllium carbide production runs were made in a pressure furnace previously used for producing beryllium meta. This furnace is shown in Fig. 1.

Each of the charges consisted of fifty pounds of a stoichiometric blend of −200 mesh beryllium powder and −325 mesh ink grade graphite. The reactions were carried on in a graphite crucible.

The pressure furnace was originally designed to pour its contents into a wart for unloading after a run. Due to this design, access to the crucible from above is inconvenient. As a result, the products of the first two carbide production runs were not segregated into surface scrapings and core material, as was done in the smaller one and four pound runs. The free carbon on these products ranged from 1.3 to 1.7% while the beryllium oxide was in the range of 1.5-1.8%.

The third run produced carbide which met the specifications established by the ANP group because the charge was removed from the furnace with post-hole diggers allowing a segregation of the surface material. The analysis of this third pilot-plant lot is shown in Table VII.

Table VII—Analysis of Beryllium Carbide from Pressure Furnace Runs in which the Core of the Product was Segregated from the Surfaces

Charge: 50 lbs. stoichiometric mixture of −200 mesh beryllium powder and −325 mesh ink grade graphite

	Brush	ANP Official
BeO	1.49%	1.05%
Free C	0.74	0.74
N_2	0.026	0.026
H_2O	0.070	0.080
Assay	60.37	---
Material Recovery	96.5	---
Good-product Yield	77.1	---

BeO content of starting beryllium powder = 1.20 %

Although the product was technically acceptable when produced by this method, the rather poor good-product yield of only 77.1% left much to be desired economically. In addition, there was an appreciable beryllium air contamination associated with the handling of the large amounts of powdered beryllium carbide produced in these runs. Because of these factors the pressure furnace was abandoned as a carbide production tool.

The successful production of beryllium carbide on a large scale was accomplished by a hot pressing technique with graphite dies. For this operation 40.48 pounds of −200 mesh beryllium powder were blended with the stoichiometric amount of ink graphite (26.68 pounds). The blend was placed in a graphite die (shown in Fig. 2) which had a 23" O.D., a 17" I.D. and was 36" high. A dead weight loading of 2 psi was

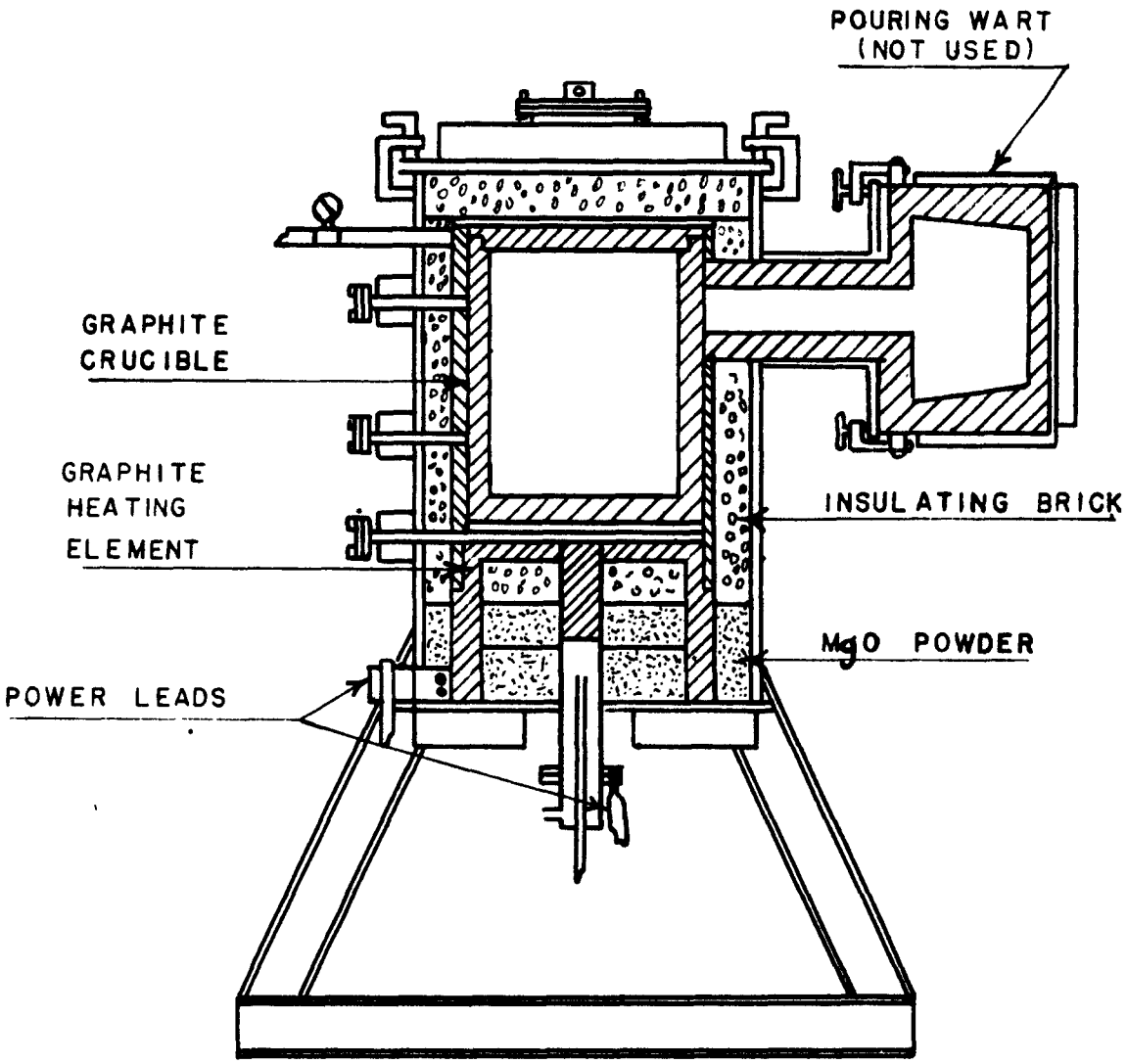

Fig. 1—Schematic Drawing of Pressure Furnace Converted to Beryllium Carbide Production.

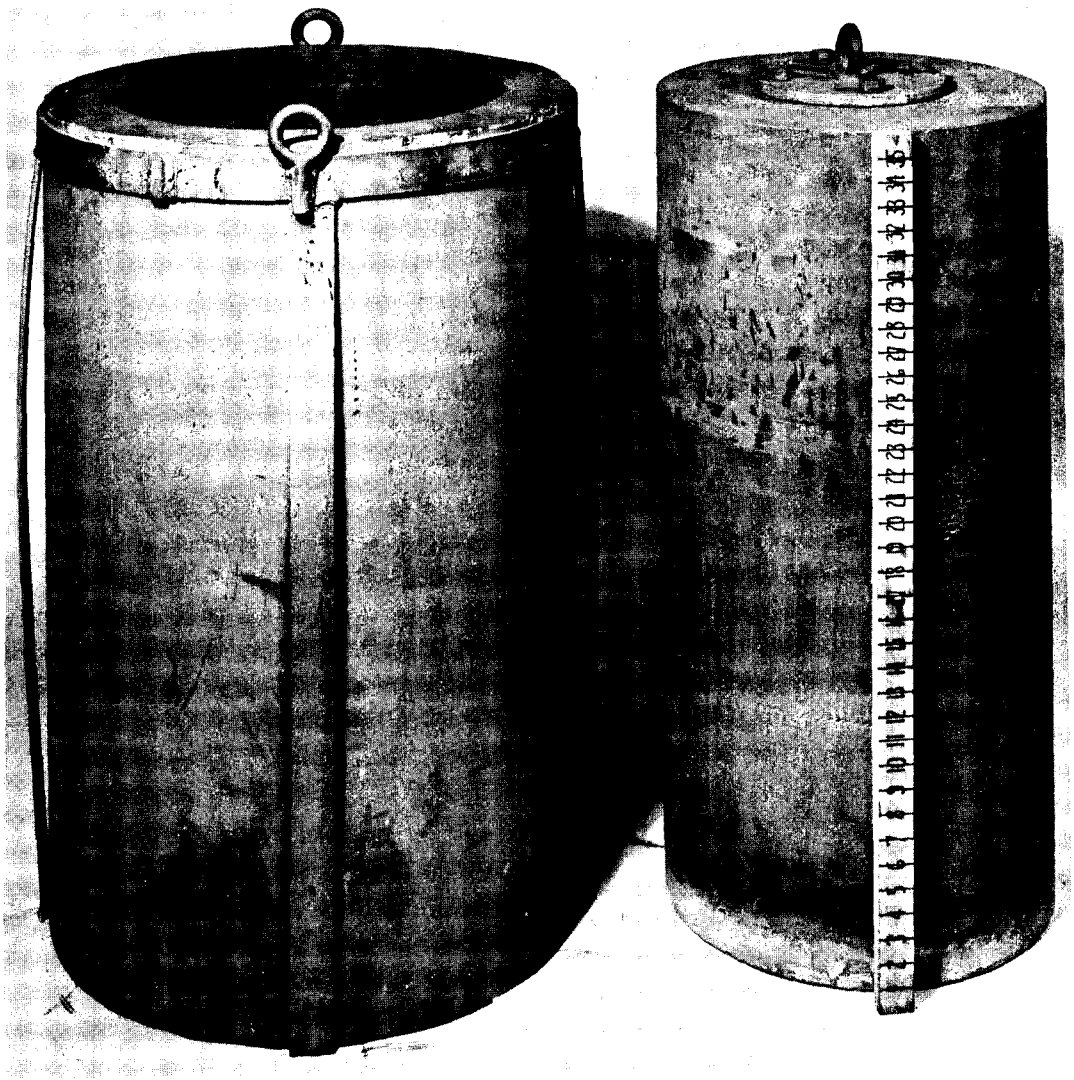

Fig. 2—Graphite Die and Ram Used in Large Scale Production of Beryllium Carbide.

placed on the charge, a vacuum of 80 microns drawn over a five hour period to prevent preferential elutriation of the reactants, and the reaction was carried out at 960° with a three hour soaking period.

After reaction, the beryllium carbide was removed as a semi-sintered compact. A material recovery of 97.9% was achieved with a good-product yield of 94.7%. The analysis of this beryllium carbide is shown in Table VIII. The analysis indicates that this beryllium carbide is superior to any other carbide produced on a large scale.

Table VIII—Analysis of Beryllium Carbide Produced by Hot-Pressing Reactants in Graphite Die

Charge: 66.5 lbs. of stoichiometric mixture of −200 mesh beryllium and −325 mesh beryllium carbide

	Brush	ANP Official
BeO	1.39%	0.72%
Free C	0.36	0.36
N_2	0.041	0.041
H_2O	0.04	0.04
Assay	60.10	---
Material Recovery	97.9	---
Good-Product Yield	94.7	---

BeO content of starting beryllium powder = 1.17 %

In Tables VII and VIII above the analyses indicated as "ANP Official" were made using the bromination method for BeO, the method upon which the specifications are based.

The indication is that even lower oxide contents may be achieved with this method as the BeO content of the starting beryllium powder in this run was high (1.17%). In addition it is felt that a lined graphite die would lower the oxide content of the product.

6. Chemical Analysis of Beryllium Carbide

The majority of the analytical methods used on beryllium carbide during this work utilized existing methods for beryllium metal analysis with modifications where necessary. As detailed descriptions of these methods have been given elsewhere (reference 4) only a brief description will be presented here.

The chemical determinations which have been usually made on beryllium carbide include beryllium-oxide, moisture, free carbon, and nitrogen. Each determination is briefly discussed below.

a. Beryllium Oxide. The weighed sample of beryllium carbide is placed in a beryllium oxide boat and heated to 650-800°C. in a stream of anhydrous hydrogen chloride gas. Beryllium chloride and methane are produced and carried out of the system by excess hydrogen chloride. The residue is weighed and dissolved to allow a colorimetric determination of the beryllium present. The precision of this method for a large number of determinations has been found to be ±15%. The major differences between oxide determinations in beryllium metal and beryllium carbide is that a slower hydrogen chloride flow rate with a longer reaction time is needed for the carbide.

b. Moisture. Helium, free of hydrogen and water, is passed over a weighed sample of beryllium carbide at 800°C. The effluent gas is passed through a tube of heated CuO which converts any hydrogen or methane to water and carbon dioxide. The water is then absorbed from the gas stream with "Dehydrite" and weighed. The precision of this determination was found to ±10%.

c. Free Carbon. For this determination, a weighed sample of beryllium carbide is dissolved in 1:1 hydrochloric acid. The solution is filtered through a pre-ignited gooch crucible containing an asbestos mat, after which the gooch is dried at 115°C. in an oven. After weighing, the gooch may be ignited and the loss in weight upon ignition taken as free carbon. For a more precise determination, the asbestos mat and carbon are transferred to a standard carbon train where the weight of carbon is calculated from absorbed carbon dioxide. The precision of this determination is ±3%.

d. Nitrogen. Nitrogen is determined by the Micro-Kjeldahl method. The sample is dissolved by refluxing with concentrated hydrochloric acid. The precision of this method has been found to be ±10%.

In addition to the above determinations, metallic impurities present in the beryllium carbide were determined spectrographically.

A method was devised by the ANP group at Oak Ridge for the determination of BeO, total carbon and the beryllium assay in a single sample. This method consisted of passing dry bromine over a weighed sample of beryllium carbide at 800°C. forming beryllium bromide and free carbon. After the bromination, the boat is weighed, re-ignited in air and reweighed to determine the total carbon by the weight loss upon ignition. The difference between the original weight of the boat and the final weight after the carbon ignition gives the weight of beryllium oxide present in the sample. The beryllium assay is measured by the weight loss during the bromination with an allowance for the moisture content.

This method when used as described above gave consistently low beryllium oxide results (e. g. 1.0% by the Br_2 method would give 1.5% by the HCl method). However, it was found that by colorimetrically determining the beryllium content of the residue and the purified silica sand upon which the sample rested in the boat, the beryllium oxide result agreed precisely with that obtained with the hydrogen chloride method. For this reason the hydrogen chloride procedure was used exclusively for the analyses reported with this work, unless otherwise stated, although the purity specifications are based on an official analysis using the bromine method.

7. Packaging and Storage of Beryllium Carbide

The beryllium carbide produced by the relatively low temperature reaction between beryllium powder and graphite powder is a material which is very hygroscopic. Moisture is apparently absorbed and retained as H_2O in the material, as well as entering into the reaction:

$$Be_2C + 2H_2O \rightarrow 2BeO + CH_4$$

The rate of moisture pick-up under varying humidity conditions is shown in Table IX. These data indicate the possible formation of a protective oxide layer on the beryllium carbide powder as the rate of moisture pick-up was materially decreased upon the second exposure to the storage conditions. As further work on this point was not undertaken, no definite conclusion may be drawn.

As a result of the hygroscopic nature of this form of beryllium carbide, special precautions must be observed in the handling, packaging and storage of the product or the advantages of purity gained in processing will be quickly lost.

The first beryllium carbide produced was stored in five gallon bottles sealed by Dekhotinsky cement, Pyseal or paraffin. These techniques were similar in that a good seal was difficult to attain and once sealed, the bottle was difficult to open.

Accordingly, a brief investigation was made of the possible use of a rubber gasket seal within the bottle cap. For this investigation the samples were stored in jars which were evacuated and filled with helium after sealing. As can be seen by the results in Table X, both lump and ground beryllium carbide was tested. Magnesium perchlorate was present as a desiccating agent in the cases indicated.

The obtained data indicate a pick-up of oxygen in all cases, including those in which magnesium perchlorate was present. However, the variation in the amount of oxygen pick-up was not great enough to indicate a superiority of any of the tested storage methods as this variation was within the accuracy limits of the analytical methods.

Table IX—Gain in Moisture Content of Beryllium Carbide Stored Under Various Conditions

	Sample Stored Under $Mg(ClO_4)_2$	Sample Stored Under 31% Rel. Hum.	Sample Stored Under 79% Rel. Hum.
Orig. Moisture Content	3.52 %	3.55 %	2.73 %
Storage Time (24 hr. days)	2.01 days	0.93 days	0.89 days
Time of Exposure to air during Analysis	0.7 min.	0.7 min.	0.7 min.
Moisture Content after Storage	0.12 %	0.26 %	0.53
Gain in Wt. Rate	4.2×10^{-5}%/min.	19.4×10^{-5}%/min.	40.9×10^{-5}%/min.
Additional storage time after Moisture Determination	---	5.48 days	5.12 days
% Moisture after Second Storage	---	0.41 %	0.56 %
Gain in Wt. Rate during Second Storage	---	4.9×10^{-5}%/min.	7.6×10^{-5}%/min.

Sample weight was one g. in all cases. Each sample was examined for moisture in its entirety, thus the moisture content during the storage period did not reach the original value during the time of test.

The standard storage method adopted was, therefore, storage in glass bottles sealed with rubber gaskets. The atmosphere within the bottle is replaced with helium after sealing. No desiccant is used with the beryllium carbide as tests with magnesium perchlorate indicate that moisture is picked up by the carbide even in the presence of this powerful desiccating agent. Accordingly, it has been concluded that the best desiccant for beryllium carbide is the beryllium carbide itself.

8. Fabrication of Beryllium Carbide

As the major function of this project was the preparation of commercial quantities of beryllium carbide, very little work was done on the fabrication of beryllium carbide bodies.

The carbide as produced by reaction under dead weight loading in graphite dies, as discussed above, is a semi-sintered mass which is removed from the dies in chunks. This material may be sliced into porous, but coherent blocks on a cut-off wheel.

Three attempts at simultaneously reacting −200 mesh beryllium powder and graphite under pressures of the order of 100 psi at about 1050°C. did not result in acceptable hot-pressed carbide shapes as in each case cracking occurred. A $4\frac{5}{16}$" square chambered die lined with molybdenum sheet was used for these tests.

The room temperature pressing characteristics of beryllium carbide were determined on a series of eight pressings 2.23" diameter by 2" high. The density vs. pressure curve for this work is shown in Fig. 3. The compacts pressed at 70 tsi and above cracked slightly when removed from the die. No binder material was added to the beryllium carbide in this work.

Table X—Variations in Oxygen Content of Beryllium Carbide Stored Under Different Conditions

Lot No.	20	22	26	26	26
Dessicant	None	$Mg(ClO_4)_2$	None	$Mg(ClO_4)_2$	None
Seal	Paraffin	Paraffin	Rubber	Rubber	Rubber
Condition of Be_2C	Ground	Ground	Ground	Ground	Lump
Shelf time	74 days	58 days	38 days	38 days	9 days with Mg $(ClO_4)_2$ · 28 days No $Mg(ClO_4)_2$
Starting Analysis					
BeO	1.85 %	1.49 %	1.40 %	1.46 %	1.40 %
Slag	0.27	0.04	0.11	0.16	0.11
H_2O	0.21	0.07	0.02	0.04	0.02
Total Oxygen (calc.)	1.37	1.01	0.92	0.98	0.91
After Storage					
BeO	1.99	1.76	1.68	1.77	1.73
Slag	0.05	0.14	0.07	0.13	N. D.
H_2O	0.14	0.18	0.27	0.01	0.62
Total Oxygen (calc.)	1.40	1.29	1.32	1.14	1.11
Oxygen Gain	2.2 %	28 %	30.3 %	16.4 %	24.2 %

All samples stored under helium.

The sample of lump beryllium carbide (lot 26) described in the right hand column above was ground before analysis. The remaining unground portion of this material was stored an additional 160 days with a rubber seal and no desiccant. At the end of this period a sample was taken from the center of a lump with $1\frac{1}{2}$" minimum thickness through the center and analyzed for BeO. This sample gave 0.90% BeO and a N.D. slag.

A preliminary investigation of the beryllium-beryllium carbide system was made by simultaneously hot pressing and reacting beryllium metal and graphite mixtures. The work was carried out in a molybdenum lined graphite die with pressures ranging from 1400 to 2500 psi at a temperature of 1050°C. for four hours. Compacts ranging from 100% Be_2C to 80% Be-20% Be_2C were made. Elevated temperature tensile tests were conducted on the 80% Be-20% Be_2C and 70% Be-30% Be_2C compacts as shown in Table XI. The corresponding tensile values for hot-pressed beryllium metal is also shown in the above mentioned table. These data indicate that the ultimate tensile strengths of these cermets are appreciably higher than the values for beryllium metal at the temperatures tested.

D. DISCUSSION

The work completed under this project makes possible the evaluation of new commercial method for the large scale production of beryllium carbide.

This process utilizing the reaction between beryllium and graphite powders may be carried out either in enclosed crucibles or in graphite dies with a dead weight loading

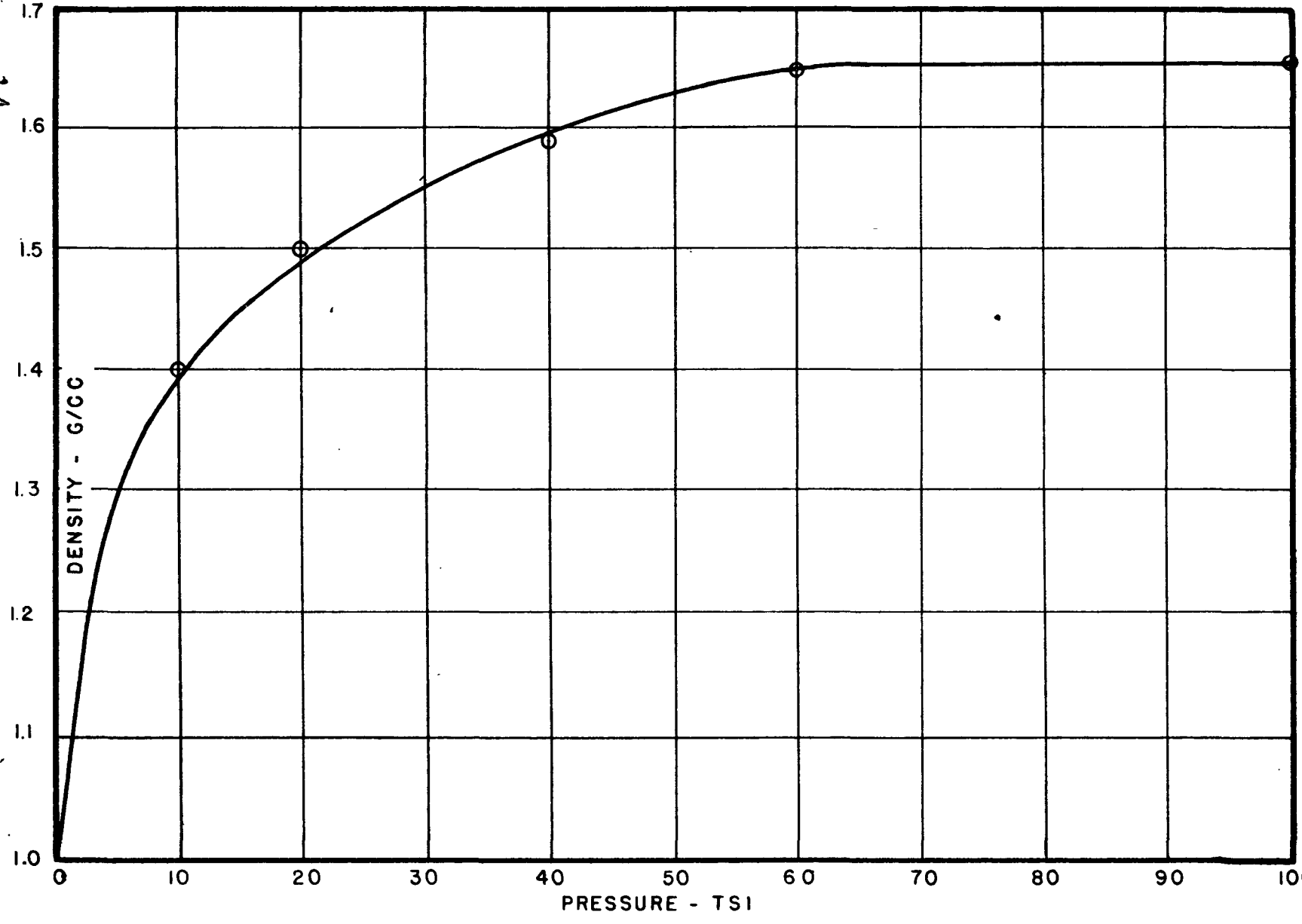

Fig. 3—Density vs Pressure for Room Temperature Beryllium Carbide Compacting.

Table XI—Tensile Properties of Be-Be_2C Cermets and Hot-Pressed Beryllium at Elevated Temperatures

Temperature of test	Ultimate Tensile Strength 1000 psi	% Elongation	% Contraction
80% Be-20% Be_2C			
600°C.	30.5	3.0	3.9
	31.4	1.7	3.9
	31.8	2.8	3.0
800°	10.8	0.0	0.2
	10.5	1.5	0.0
	10.5	2.2	0.4
950°	4.7	1.8	0.0
	4.6	2.5	0.0
975°	3.5	2.1	0.0
70% Be-30% Be_2C			
600°	24.4	1.0	1.1
	(Hot-pressed QMV. Each value the average of three tests on one lot.)		
100% Be			
600°	22.3	23.2	38.8
	19.4	16.1	18.6
	19.8	14.4	20.5
800°	6.4	6.3	5.6
	6.0	7.9	7.3
	6.5	9.5	6.8
900°	2.3	6.3	2.7
	1.4	9.6	3.0
	1.9	4.5	6.3
950°	1.9	4.9	3.1

The principle advantages of this process lie in the low temperatures involved in the reaction as contrasted to the previous method of production which reduced beryllium oxide by carbon. By operating in the neighborhood of 1000°C., instead of 2000°C. as required in the oxide method, the furnacing problems for large-scale production become relatively simple since the size limitations of induction heating are not encountered.

In addition, a material improvement of product purity is achieved in that the rate of formation of beryllium nitride is apparently very much slower at the lower reaction temperature. In the carbide produced from the oxide this compound is a major impurity, ranging from 2 to 3%. In the low temperature carbide produced by reacting beryllium and graphite powders the beryllium nitride content has been 0.05% or less.

The comparative cost of producing beryllium carbide from the oxide and from the first-order powder reaction both in a crucible and a die is shown in Table XII. It will be noted that although beryllium in the form of the oxide is much cheaper than the −200 mesh metal powder, the beryllium carbide produced from beryllium oxide has a manufacturing cost in the neighborhood of $64 per pound while the manufacturing cost of beryllium carbide from beryllium metal is $55 or $47 depending upon the equipment used. This apparently incongruent situation arises from the fact that 100 lbs. of beryllium metal and carbon in the stoichiometric quantities react to form 100 lbs. of beryllium carbide product. However, 100 lbs. of a stoichiometric mixture of beryllium oxide and carbon react to form only 35 pounds of beryllium carbide assuming 100% reaction. Moreover, a container in which 100 pounds of beryllium powder-carbon powder mixture may be reacted with ease will contain at the most only about 75 pounds of the beryllium oxide-carbon mixture during the reaction, as the evolved carbon monoxide will "fluff up" the charge considerably. Consequently, the cost of beryllium carbide from beryllium oxide is raised greatly because of the labor and service charges. These charges, it will be noted, are essentially the same as those for the beryllium metal-graphite reaction per run, but because of the low poundage of beryllium carbide produced per run, increase the cost of beryllium carbide per pound very appreciably.

Table XII—Cost Analysis for Producing Beryllium Carbide

	Be-Graphite Powder Reaction		BeO-Carbon Reaction
	Crucible	Graphite Die	Induction Furnace
Maximum capacity	100 lbs.	140 lbs.	30 lbs.
Assumed material recovery	100 %	100 %	80 %
Good-product recovery	80 lbs.	134 lbs.	24 lbs.
Raw material cost	$3,487.80	$4,882.92	$400.00
Labor			
Operational	14 man hrs.	60 man hrs.	36 man hrs.
Analytical	70 man hrs.	70 man hrs.	70 man hrs.
Labor, Overhead Service Charges	$840	$1,300	$1,060
Packaging, Handling, Delivery	$100	$125	$30
Total Cost	$4,427.80	$6,307.92	$1,550
Cost/pound	$55.35	$47.07	$64.58

Above cost based on: −200 mesh Be powder at $58.13/lb.
G.C. Grade BeO at $9.20/lb.
Maintenance, power and graphite costs are not included as these are essentially equal and do not appreciably add to the cost.

Capacity figures are based on equipment at the Brush Beryllium Company.

The most advantageous method of producing beryllium carbide is, therefore, the beryllium powder-graphite powder reaction both from the technical viewpoint with the elimination of the nitride impurity and from the economic viewpoint with the lowered manufacturing cost due to increased equipment capacity.

While the production of beryllium carbide from the component powders in crucible equipment is feasible and decidedly more advantageous than the oxide reaction, the process involving reaction in graphite dies is to be considered the most practical from both an economic and technical viewpoint.

The advantages of reacting in dies over the crucible reaction include:

1. Increased product yield.
2. Increased quality of product through a lowering of the free carbon content and a potential lowering of the beryllium oxide content through the use of molybdenum lined dies.
3. Increased equipment capacity.
4. Lowering of the beryllium contamination of the air which accompanies the handling of the crucible produced powder product.

E. CONCLUSIONS

The following conclusions may be drawn from this work:

1. Beryllium powder and graphite powder will react at temperatures in the neighborhood of 1000°C. to form the purest beryllium carbide produced in large amounts to date.
2. The relatively low temperature operation involved in the production of beryllium carbide from beryllium and graphite powders does not permit the formation of beryllium nitride, a major impurity in beryllium carbide produced from beryllium oxide at 2000°C.
3. The best grade of beryllium carbide made by the beryllium powder-graphite powder is produced when the exact stoichiometric amounts of both reactants are present with an allowance for the non-reacting beryllium oxide present in the beryllium powder, as no attempts at impurity removal from the bulk of the product have been successful.
4. The temperature at which the exothermic reaction between beryllium powder and graphite powder is initiated is a function of the particle size of the beryllium powder. For −200 mesh beryllium powder and −325 mesh graphite this temperature is about 910-935°C. With coarser powders the reaction temperature is increased.
5. The reaction may be satisfactorily carried out in graphite. However, for minimum beryllium oxide content, it is recommended that a molybdenum liner be used with the graphite container.
6. The reaction may be carried out in either a crucible or a large graphite die with dead weight loading. The latter procedure is to be recommended as the product yield, product purity and equipment capacity are increased with this procedure while any beryllium contamination of the air accompanying the process is greatly decreased due to the less powdery nature of the product.

F. RECOMMENDATIONS

1. It is recommended that future requirements of beryllium carbide be produced exclusively by the low temperature beryllium powder-graphite powder reaction. This reaction should be further studied along the following lines.
   a. The preliminary investigation of the maximum beryllium powder particle size should be extended to coarser fractions and higher temperatures to determine the point at which beryllium nitride formation becomes excessive enough to cancel the benefit obtained in using the lower oxide content, coarser powders.
   b. Large scale runs using low oxide −200 mesh beryllium powder and molybdenum lined graphite dies should be made in order to determine the minimum beryllium oxide content which can be achieved with the reaction between fine powders.
2. A more thorough investigation should be made of the possibilities of hot-pressing beryllium carbide shapes to near full density by starting with beryllium and graphite powders and reacting and pressuring simultaneously.

3. The storage conditions and shelf life of beryllium carbide should be studied more extensively to determine the best way of keeping pure beryllium carbide once such material is produced. In addition the possible formation of protective oxide films should be investigated.

4. As there is a small, but steady, demand for beryllium carbide blocks and shapes for a variety of nuclear experiments, it is recommended that a brief study be made of protective coatings for such material which is usually supplied in the subdensity or porous condition.

G. SUMMARY

Beryllium carbide has been produced successfully in lots up to sixty pounds per run with a potential capacity of 140 pounds per run by utilizing the reaction between beryllium powder and graphite powder. This material is among the purest carbide produced to date as the oxide content was 0.72%, free C 0.37%, nitrogen 0.04% and water 0.04% with a beryllium assay of 60.10%.

The reaction between −200 mesh beryllium powder and −325 mesh ink-grade graphite proceeds rapidly with the evolution of heat at about 910-935°C. As the particle size of the beryllium powder increases, the reaction temperature also increases with the additional feature that heating beyond the initiation of the reaction is necessary to carry the reaction to completion.

Large scale production has been carried out both in crucibles and in graphite dies under dead weight loading. The latter procedure is recommended as the product is recovered in large chunks which allows for the easy removal of surface impurities thus increasing the yield and lowers the beryllium contamination of the air associated with handling the powdered material obtained in crucible reactions.

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Report Number	Card Classification	Code	Report Category	Set	Journal
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Brush Beryllium Co., Cleveland.

THE PRODUCTION OF HIGH-PURITY BERYLLIUM CARBIDE. J. G. Theodore, W. W. Beaver, A. Dolance, and A. J. Stonehouse. Oct. 15, 1952. 20p. Contract AT(30-1)-541. OTS.

(Decl. Sept. 21, 1960, Rep. (me))

Date Cataloged w/Initials 11/2/60gs a | $3.30(ph), $2.40(mf) OTS

I. Personal Author(s) (4)
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Short title: Production of Pure Be_2C

095,081 Beryllium carbides -- production of high-purity

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