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RESEARCH AND TECHNOLOGY DIVISION
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Project No. 7351, Task No. 735104

(Prepared under Contract No. AF 33(616)-7065 by
Nuclear Metals, Inc., West Concord, Massachusetts)

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FOREWORD

This report was prepared under USAF Contract No. AF 33(616)-7065 with Nuclear Metals, Inc., West Concord, Massachusetts, as the prime contractor. The contract was initiated under Project No. 7351, "Metallic Materials," Task No. 735104, "Beryllium and Beryllium Alloys." The work was administered under the direction of the Metals and Ceramics Division, Air Force Materials Laboratory, Research and Technology Division, with Mr. K. L. Kojola and Capt. P. S. Duletsky acting as project engineers.

The work reported in this volume is divided into seven (7) sections. Section I is an Introduction to the research covered by this volume. Section II, "Preparation and Evaluation of High-Purity Beryllium," was prepared by E. D. Levine, J. P. Pemsler, and S. H. Gelles of Nuclear Metals, Inc., West Concord, Massachusetts. Section III, "Preparation and Evaluation of High-Purity Beryllium Single Crystals Grown From the Melt," was prepared by S. H. Gelles of Nuclear Metals, Inc. Section IV, "Fine Beryllium Powder Made by Attritioning," was prepared by A. S. Bufferd, R. Widmer, and N. J. Grant of New England Materials Laboratory, Inc., Medford, Massachusetts. Section V, "Preparation of Ultra-Fine Beryllium Powder," was prepared by P. L. Raymond of National Research Corporation, Cambridge, Massachusetts. Section VI, "Fabrication and Evaluation of Ultra-Fine-Grained Beryllium Powders," was prepared by A. K. Wolff and S. H. Gelles of Nuclear Metals, Inc.

This report covers work conducted from 17 June 1959 to 1 October 1963.

The Air Force gratefully acknowledges the assistance provided by Dr. A. R. Kaufmann of Nuclear Metals, Inc. in editing this report.

ABSTRACT

The projects reported in this volume cover a portion of the work conducted on the Beryllium Research and Development Program and were primarily concerned with effects of grain size and purity of beryllium.

Section II describes the efforts to produce the purest beryllium possible by double vacuum distillation. The distilled beryllium when converted to powder and subsequently extruded exhibited greater bend ductility than any of the other forms of less pure beryllium utilized in the evaluation.

In Section III, the work involves the evaluation of the ductility and critical resolved shear stress for basal slip of cast single crystals of Pechiney SR grade and single distilled beryllium. The data were compared with previous work on cast commercial grade and zone-refined single crystals.

Sections IV and V were aimed at achieving finer grain size powder, while minimizing contamination, than had ever been produced. In Section IV, the powder of particle sizes less than 5 microns was produced by improved attritioning methods. Section V reports the attainment of powder sizes of approximately 300 angstroms by evaporation and condensation. Section VI was concerned with the consolidation and evaluation of powders produced in Section V. The hot pressed powder had exceptionally high hardness and was very brittle, prohibiting the preparation of mechanical test specimens.

This technical documentary report has been reviewed and is approved.

I. PERLMUTTER
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I. INTRODUCTION

Recent investigations of the mechanical properties of beryllium have demonstrated that purity, grain size, and texture are the most important considerations in obtaining better beryllium. The programs of work contained in this volume are concerned primarily with the first two subjects.

The work described in Section II led to the production of the purest beryllium ever achieved through the use of a double distillation process. This material and a number of other forms of less pure beryllium were converted to powder, consolidated by extrusion, and evaluated with tensile and bend tests on a small scale. Fairly convincing evidence was obtained that higher purity leads to greater ductility in polycrystalline material. In addition, beryllium was produced by double distillation and zone refining with the intention of converting this to polycrystalline metal. The aim of this endeavor was to determine if high purity material subsequently subjected to zone refining would have unusually high ductility in polycrystalline form. The contract period came to an end before this work was completed.

The investigation described in Section III was aimed at determining if single crystals of beryllium, produced by solidification from the melt, having a purity intermediate between that of commercial material and zone refined material, would have intermediate values of ductility. The results demonstrated that ductility was greater than that of commercial material and less than that for zone refined and the critical resolved shear stress for slip on the basal plane was less than the values for commercial material and greater than zone refined. The mechanical properties of the crystals made from the melt did not correlate exactly with the properties of zone refined crystals of similar purity.

Sections IV and V were aimed at achieving finer grain size than had been previously obtained by making unusually fine powder which would not be excessively contaminated with oxygen or other impurities. This work was motivated by the fact that cast beryllium, which is very low in oxide, cannot be converted to an extremely fine grain size by working and annealing. Oxide films which appear on powdered beryllium are useful in preventing grain growth and, for this reason, it was not felt necessary that the ultra-fine powders have extremely low oxygen content. (A detailed study of the distribution of oxide in powder metallurgy beryllium is to be found in Volume VI.) Section IV of this volume was concerned with achieving powder particles in the range of 1 to 5 microns using an improved attritioning method. Section V employed an evaporation and condensation technique which has produced powders of other metals, such as aluminum, in sizes less than 0.1 micron. Both of these programs had difficulty with avoiding contamination, but sufficient work was done to indicate that these problems could be satisfactorily solved if further work was carried out. No usable material was produced before the end of the contract period.

Section VI was concerned with the consolidation and evaluation of the fine powders which were to have been produced in Sections IV and V. This undertaking required the development of specialized techniques to avoid contamination,

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especially for the ultra-fine powder produced by evaporation which was found to be extremely pyrophoric. Equipment for this purpose was put into operation and sufficient work was done to indicate that the problems encountered could be solved. Some data concerned with particle size and purity of material produced in Sections IV and V are reported here. No mechanical properties were obtained since the contract ended before suitable material was available.

II. PREPARATION AND EVALUATION OF HIGH-PURITY BERYLLIUM

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(Nuclear Metals, Inc., West Concord, Massachusetts)

A. Abstract

Previous purification studies (Ref. 1) indicated that beryllium of exceptionally high purity could be obtained by a vacuum-distillation process. Assessment of the mechanical behavior of this material was hampered by the difficulty in fabricating specimens of suitable metallurgical quality. In this program, the distribution of residual impurities in distilled beryllium was studied in detail, and fabrication procedures were developed that resulted in the preparation of samples having a fine, uniform, recrystallized grain structure. These procedures involved attritioning to powder and extruding into flats.

Impurity studies revealed that in addition to trace amounts of soluble impurities, insoluble particles containing iron and silicon exist, and that these particles probably limit ductility severely. A reduction in both soluble and insoluble impurities was obtained by performing a second distillation.

Mechanical property studies revealed that double-distilled beryllium exhibits considerably greater three-dimensional ductility than material of lower purity. In wide-sheet bend tests, conducted at room temperature, bend angles at fracture of 50° to 70° (three percent tensile strain in outer fibers) were observed.

B. Introduction

The purpose of this program was to prepare beryllium of exceptionally high purity by means of vacuum distillation and to evaluate the mechanical properties of such material in order to determine if significant improvements in ductility can be obtained in polycrystalline beryllium by purification.

This report presents a description of work performed in the second part of the program. During the first part (Ref. 1), an apparatus was constructed which permitted the distillation of liquid beryllium, at a vacuum of 10^{-6} mm Hg, onto a tantalum collector maintained at 1060-1150°C. With this apparatus, it was possible to prepare beryllium of purity levels previously unattained. The

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development of special spectrophotometric techniques was required in order to determine the concentration of specific impurities. An analysis of a typical distillate, compared to that of vacuum-melted Pechiney flake (CR grade), which was employed as the starting material for distillation, is given in Table 1.

Evaluating the mechanical properties of distilled beryllium proved to be a difficult task. The as-distilled product, although consisting of a coherent polycrystalline mass, was quite porous and large-grained. In order to obtain test samples of suitable metallurgical quality, it was necessary to develop consolidation procedures that would produce densification and permit some control over grain size and preferred orientation, while maintaining the high purity characteristic of as-deposited material. Initial attempts to fabricate distilled beryllium, which included direct rolling of distilled material and also vacuum melting followed by extrusion and rolling, were only partially successful in controlling the above variables. The grain size of the test samples remained relatively large and non-uniform, and the cold work imparted by fabrication was quite inhomogeneous. Some grains remained essentially undeformed, while others received sufficient cold work to undergo recrystallization during subsequent annealing.

Wide-sheet bend tests performed on material fabricated by the above techniques indicated little ductility. The poor mechanical properties were attributed in part to insufficient control of metallurgical parameters during fabrication.

Another factor limiting ductility was felt to be the presence of residual impurities in distilled beryllium. Tangible evidence of such impurities was observed in the form of second-phase particles, approximately one micron in diameter, on fracture surfaces. Occasional samples that exhibited some ductility contained appreciably fewer particles than did samples of low ductility. Similar particles have been observed on zone-refined single crystals of beryllium subjected to only one or two zone-refining passes and which exhibited little ductility (Ref. 2). On the other hand, very few particles are observed on multi-pass crystals which generally exhibit considerable ductility. It appears likely, therefore, that the presence of such particles has a serious effect on the mechanical properties of beryllium.

In the second part of the program, increased efforts were devoted to learning more about the nature of the impurities in distilled beryllium. Information so obtained was then applied to experiments on further purification and on new fabrication procedures to obtain specimens of high metallurgical quality.

C. Study of Impurities in Distilled Beryllium

In attempting to characterize impurities in distilled beryllium, one needs to consider not only the total content of specific impurities, as determined by chemical analysis, but must also be concerned with the structural distribution of impurities. For example, it is quite important to determine the composition and source of the second-phase particles which appear to have such a serious effect on ductility. In addition, it is necessary to obtain information on

TABLE 1

IMPURITY CONTENTS OF VACUUM-MELTED PECHINEY FLAKE (CR GRADE) AND DISTILLED BERYLLIUM

Element	Concentration, in ppm by weight	
	Flake	Distilled
Fe	160	3
Ni	130	2
Cr	20	1
Mn	20	5
Si	60	12
Al	55	20
Cu	10	5

residual impurities in solid solution, since single crystal studies have shown that several features of the plastic deformation of beryllium are directly related to solute concentration (Ref. 3).

1. Chemical Analysis

In the first part of the program (Ref. 1), spectrophotometric techniques for the determination of iron, nickel, chromium, manganese, aluminum, silicon, and copper were developed which permitted the quantitative determination of residual amounts of these elements when present to the extent of only a few parts per million. Since spectrographic analysis indicated that probably no other metallic impurities were present in more than trace quantities, further development of analytical techniques for metallic impurities was limited to finding a method for the determination of tantalum.

Tantalum was of concern because of the possibility of contamination from the collector during distillation. An electron microbeam probe analysis* of a beryllium-tantalum diffusion couple, annealed at 1150°C, which is approximately the collector temperature during distillation, revealed the existence of a 50-100 micron layer of a phase corresponding very closely to $TaBe_{12}$. The tantalum gradient on each side of the layer was very steep, indicating that very little tantalum actually diffused into the beryllium. These observations, however, suggested that some tantalum contamination might exist on the outside surface of the distilled cones. Microbeam probe scans of a cone surface revealed no evidence of contamination by diffusion, but did reveal the presence of a few small particles from the tantalum collector that had adhered to the cone after the collector had been peeled off.

It was necessary, therefore, to etch the cones in HCl prior to further treatment to undercut the adhering tantalum particles. In order to measure the completeness of the etching procedure, an analytical technique for tantalum was required. Accordingly, a method was developed** which involved the liquid extraction of tantalum in methyl-isobutylketone and the photometric determination of tantalum as tantalum phenylfluorene. The minimum detection limit of the technique is 2 ppm.

Analyses for tantalum were performed on Pechiney flake beryllium and on samples of distilled beryllium in the etched and unetched conditions. These samples were taken from a region of the cone adjacent to the tantalum collector, so the tantalum contents were higher than that of the beryllium deposit as a whole. The results are presented in Table 2. They indicate that tantalum is effectively removed by etching.

With respect to the determination of nonmetallic impurities, experimental efforts were directed to the determination of oxygen in distilled beryllium. The problem of oxygen in beryllium has been one of major interest for several years, but its solution has been hampered by the absence of analytical techniques sensitive below 1000 ppm. Recently, however, some new

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* Performed at Advanced Metals Research Corporation, Somerville, Massachusetts.
** This work was performed by E. Pollock.

TABLE 2

DETERMINATION OF TANTALUM IN BERYLLIUM

Material	Condition	Tantalum (ppm)
Pechiney flake		2
Distillate No. 16, material immediately adjacent to collector	Unetched	11
Distillate No. 16, material slightly removed from surface adjacent to collector	Unetched	7
Distillates No. 28 and No. 29, material adjacent to collector	Etched	2

techniques have shown some promise of application to small quantities of oxygen in beryllium. Examples of such techniques are fast neutron activation, gamma activation, and micro-vacuum fusion.

Samples of beryllium purified by distillation and by zone-refining, plus control samples of vacuum-melted Pechiney CR flake, were analyzed by the above techniques at the following laboratories: UKAEA Atomic Weapons Research Establishment, Aldermaston, United Kingdom; UKAEA Atomic Energy Research Establishment, Harwell, United Kingdom; CEN Saclay, Gif-sur-Yvette, France; and Texas Nuclear Corporation, Austin, Texas. A summary of the oxygen determinations is given in Table 3.

It is difficult to draw definite conclusions from these data, since the techniques employed differed widely, and since samples of similar material were not all taken from the same piece. In addition, subsequent work at Aldermaston by fast neutron activation has shown that a large proportion of total oxygen is restricted to surface layers. By etching the samples after irradiation and before counting, the Aldermaston values of Table 3 were reduced by 30-40 ppm. Analysis of an additional sample that had been prepared by performing six zone-refining passes on distilled beryllium gave 70 ppm without etching and only 5 ppm with the surface removed.

Tentative conclusions are that the oxygen content of distilled beryllium is approximately 100 ppm, a value probably somewhat less than that in vacuum-melted Pechiney CR flake, and that there is indication that floating zone-refining may produce an additional large reduction in oxygen. This would probably be due to the elimination of the crucible as a source of oxygen contamination. Much analytical development remains to be done, however, before completely reliable information can be obtained.

2. Studies of Impurity Phases:

Extensive efforts were made to determine the identity and source of the second-phase particles that are observed on fracture surfaces of distilled beryllium. An example of the appearance of these particles is shown in Figure 1. Fracture surfaces of a large number of samples of various histories were examined metallographically and were analyzed with the electron microbeam probe.

These analyses revealed that silicon and iron are the major components of the second-phase particles, with silicon being the primary impurity. Aluminum and sulfur, previously suspected to be present in significant quantities (Ref. 1), were found actually to be present only in minor amounts and in only a few precipitate particles.

Particles were also observed in beryllium subjected to a second distillation, but these appeared to be fewer in number than is generally observed in single-distilled beryllium.

Similar particles, in much greater density, were observed on fracture surfaces of the starting material for distillation, vacuum-melted Pechiney CR flake. An example is shown in Figure 2. Microbeam probe analysis revealed

TABLE 3

OXYGEN ANALYSES OF HIGH-PURITY BERYLLIUM

Material	Fast Neutron Activation		Micro-vacuum Fusion	Gamma Activation
	Aldermaston	Texas Nuclear	Harwell	Saclay
Vacuum-melted Pechiney CR flake	55	300 ±25	160	160 ±50
Distilled beryllium	90-140	80 ±30	60	90 ±40
Distilled and vacuum melted beryllium	65-90			
Zone-refined Pechiney CR				
1 - pass			260	10 ±5
2 - pass			300	7 ±5
3 - pass			140	30 ±10

500X Bt. Lt. B-462b

Fig. 1 - Second-phase particles on fracture surface of distillate No. 17.

750X Bt. Lt. B-460

Fig. 2 - Second-phase particles on fracture surface of vacuum melted Pechiney CR flake.

that here, also, silicon and iron are the major components of the particles. Small amounts of aluminum and nickel were also found. It could not be determined whether these particles are identical to those in distilled beryllium.

The above analyses are qualitative in nature, because of the small size of the particles relative to the electron beam. Some observations were made on a fracture surface of a sample from the last portion to solidify of a 5-pass zone-refined bar prepared from distilled beryllium, in the hope that particles large enough for a quantitative analysis would be present. However, as shown in Figure 3, although the particle density was appreciably higher than in as-distilled material, little coalescense or growth occurred. Again, silicon and iron were found to be the principal impurities.

X-ray diffraction studies were also performed in an attempt to obtain additional information on the second-phase particles. Such studies were difficult to perform because of the small amount of insoluble material in distilled beryllium. Best results were obtained by powdering the distillate in a beryllium mortar with a beryllium pestle and obtaining a Debye-Scherrer pattern with a 19 cm camera. One distillate examined in this way was found to contain a face-centered-cubic phase with a lattice parameter of approximately 10.3Å. The composition of this phase could not be determined.

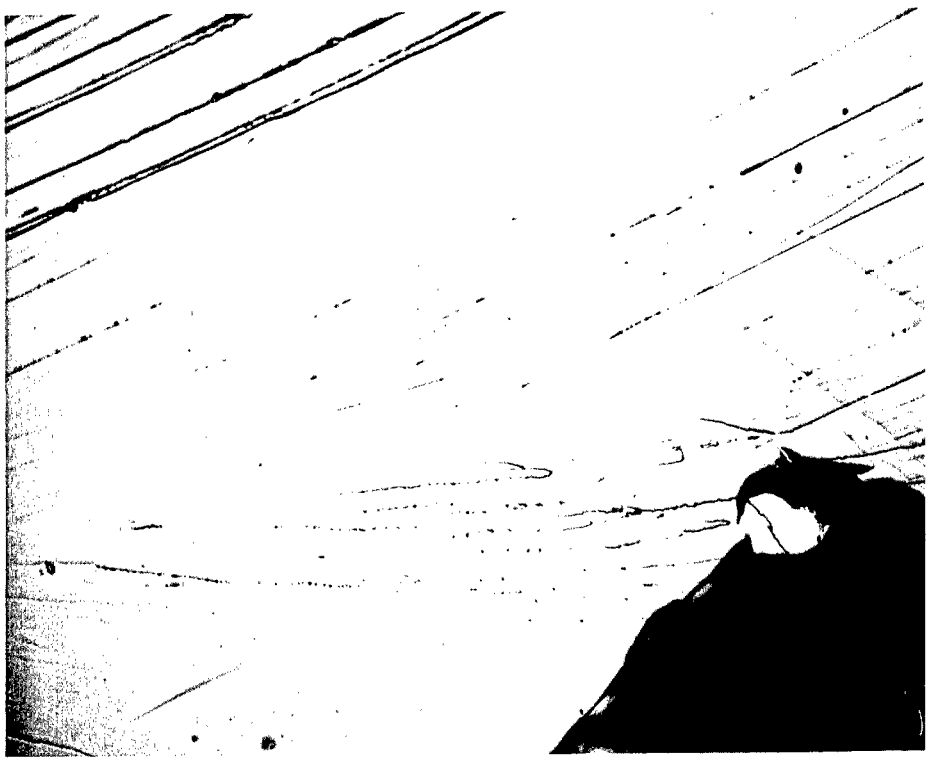
A similar phase has been found by Niebylski (Ref. 9) at the Ethyl Corporation on double-distilled beryllium supplied by Nuclear Metals. In addition, Niebylski found a compound which indexed as face-centered-cubic having a lattice parameter A_o = 6.07Å. This may be in the family of compounds discussed by Carrabine (Ref. 10).

Additional experiments were performed on samples taken from the last portion to solidify of zone-refined bars. These are the samples in which impurity phases become concentrated. No bars made from distilled beryllium were available for these experiments, so studies were performed on crystals made from Pechiney beryllium. Selective chemical dissolution, employing a bromine-methanol solution (Ref. 4), was used to dissolve the beryllium matrix, leaving a white residue of insoluble material for X-ray diffraction. A Debye-Scherrer pattern revealed the existence of BeO, Be_2C, and Si. Since the starting material for this bar was Pechiney beryllium, no conclusions on distilled beryllium can be made.

Specimens of distilled beryllium are also being examined by selected-area electron diffraction by the Pechiney Company in order to determine the structure of the second-phase particles.

3. Resistance Ratio Measurements

In order to obtain information on the relative amounts of total soluble impurities in material purified under different conditions, the ratio of electrical resistance at room temperature to that at 4.2°K was measured. This quantity, commonly called resistance ratio, is primarily controlled by the concentration of impurities in solid solution, and is affected to only a minor extent by changes in structure and orientation (Ref. 5). The resistance ratio



500X Bt. Lt. B-465

Fig. 3 - Second-phase particles on fracture surface of last portion to solidify in a 5-pass zone-refined bar prepared from distilled beryllium.

is generally very sensitive to changes in purity, values ranging from near unity for very impure metals to $> 10^4$ for ultra-high purity metals (Ref. 6).

Electrical resistance measurements were performed by the D.C. current and potential method shown schematically in Figure 4. The D.C. source consisted of five 6-volt batteries connected in parallel. Three banks of resistors were used to regulate the current. By proper selection, currents of 1, 4.5, 9, and 34 amperes could be passed through the sample. Current was determined by measuring the voltage drop across a standard resistor. Voltage drops were measured by means of a Rubicon potentiometer in conjunction with a galvanometer. At the 34-ampere current level, the voltage drop was measured by means of a Keithly 150A microvolt-ammeter.

Heavy flexible current leads were soft soldered to the ends of the sample. Voltage probe leads were wrapped tightly around, and electrical contact was made by coating the wire and adjacent sample surface with silver conducting paint. The sample with leads attached was placed in and near one end of a long micarta tube. One current lead and the voltage probe leads were passed through the center of the tube, and the other current lead was taped to the outside of the tube. A loop in the external current lead allowed for expansion and contraction during heating and cooling.

Measurements at 4.2°K were performed by immersing the sample assembly in a 25-liter liquid helium flask.

Large increases in resistance ratio were observed on purification of beryllium. Data on commercial grades of beryllium are presented in Table 4. Distillation, employing Pechiney CR flake as the starting material, increases the resistance ratio from 10 to several hundred. As shown in Figure 5, an impurity gradient exists along the axis of the distilled cone, higher values of resistance ratio being observed in the regions of higher deposition temperature. These results agree well with chemical analysis, which indicates that manganese segregates toward the cooler portions of the cone.

The data shown in Figure 5 are for single and double distilled beryllium and vacuum-melted distilled beryllium that had been prepared during the first part of the program. Re-distillation appears to reduce the gradient somewhat, in addition to raising the general purity level. The highest resistance ratio obtained for re-distilled beryllium was 900; that for single distilled, 750.

Since the thickness of the deposit is smallest near the top of the cone, the average resistance ratio of a deposit would be expected to correspond to that at a position somewhat below the mid-height of the cone. Resistance ratios for vacuum-melted distillate are considerably lower (around 140) than those predicted on such a basis. Apparently, some contamination is introduced by vacuum melting, probably from the BeO crucible. It should be noted, however, that the resistance ratio of vacuum-melted distilled beryllium is still an order or magnitude greater than that observed in vacuum-melted beryllium of commercial purity.

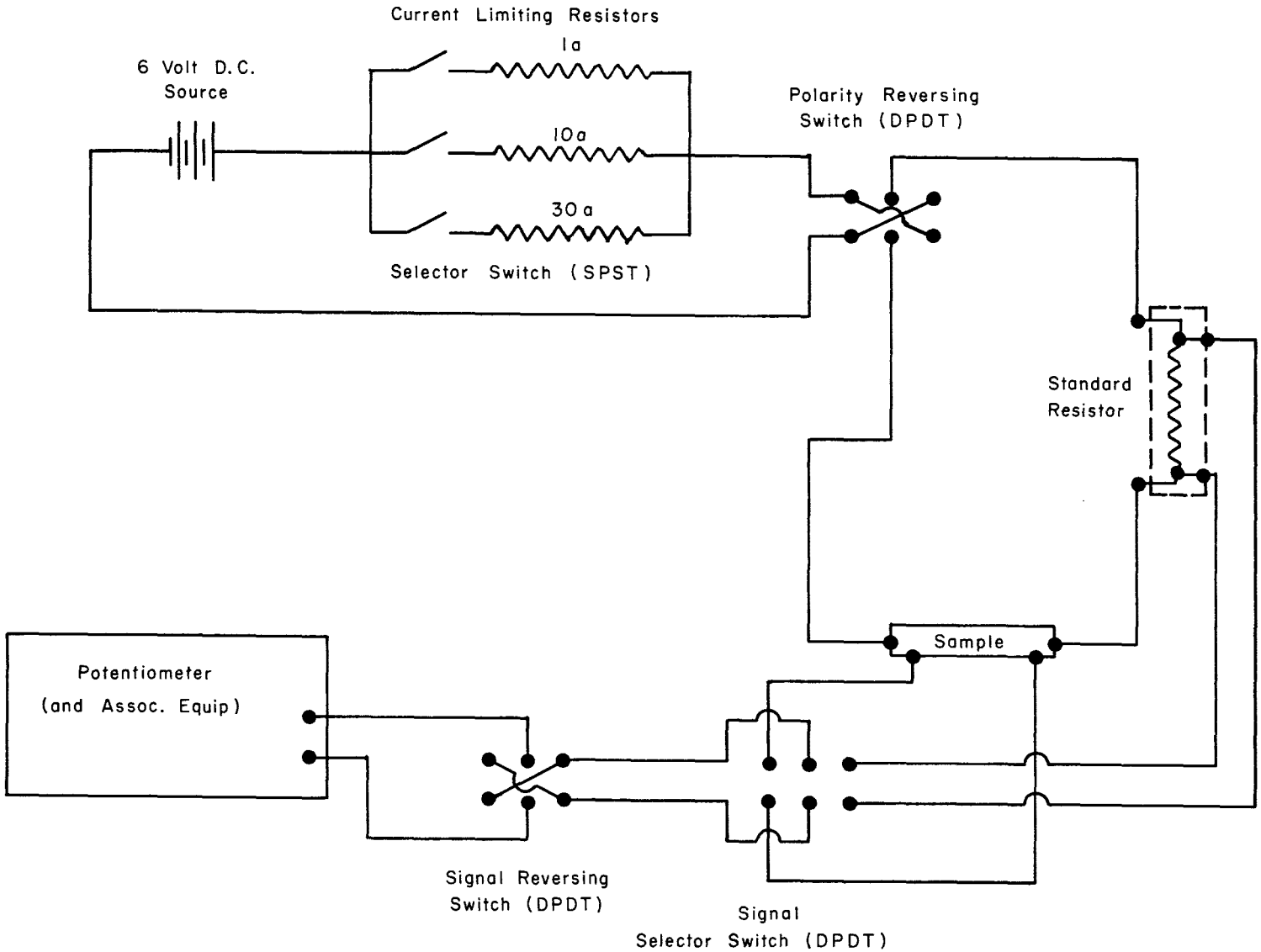


Fig. 4 - Simplified schematic of resistivity apparatus. Drawing No. RA-2500.

TABLE 4

RESISTANCE RATIOS OF COMMERCIAL GRADES OF BERYLLIUM

Material	$R_{300°K}/R_{4.20°K}$
Vacuum-melted Brush QMV	2.5
Vacuum-melted Pechiney CR flake	10
Vacuum-melted Pechiney SR flake	50

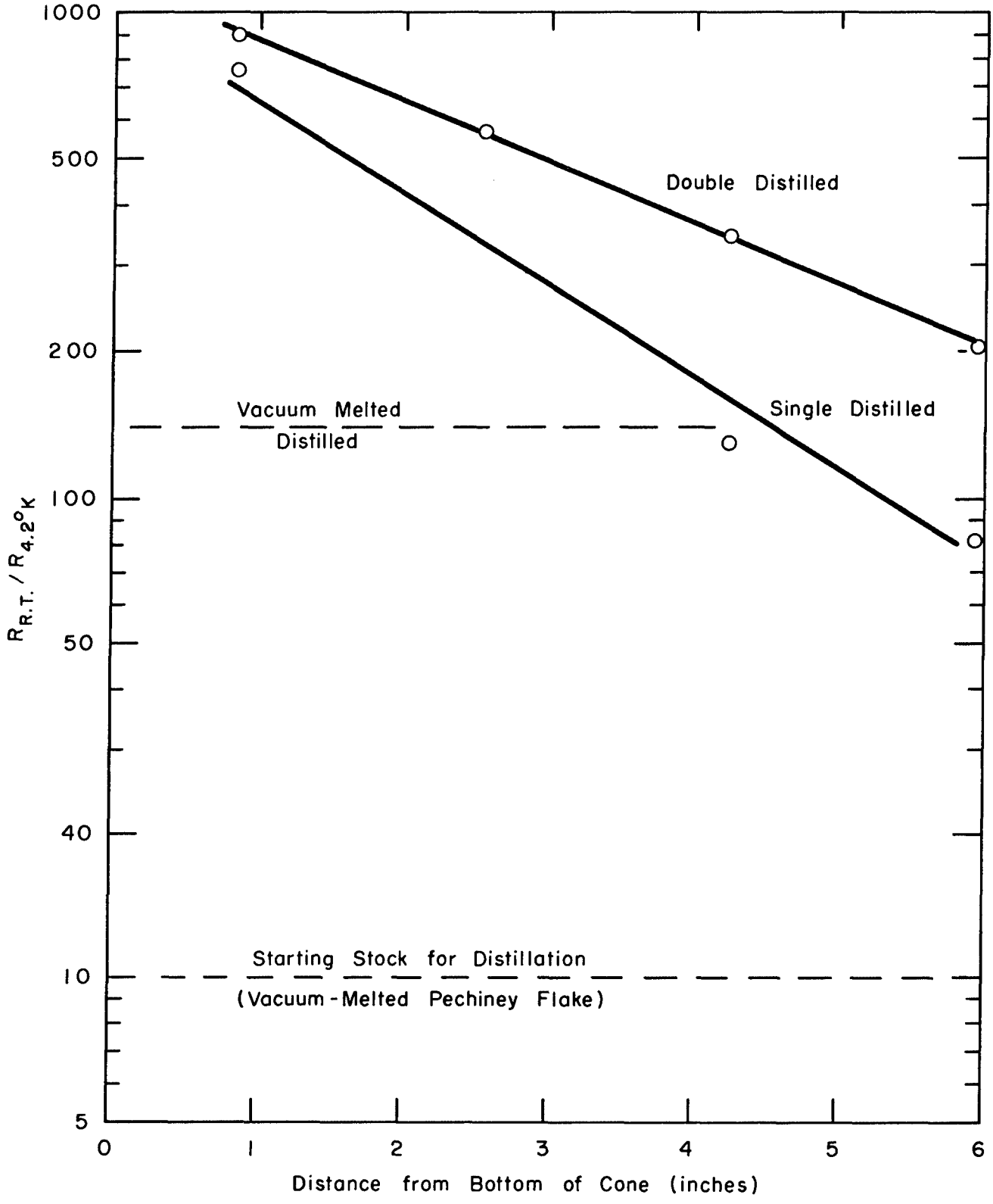


Fig. 5 - Resistance ratio data for distilled beryllium. Drawing No. RA-2317.

D. Preparation of High-Purity Beryllium for Mechanical Evaluation

Observations on the amount and distribution of second-phase particles in distilled beryllium and measurements of resistance ratio, described above, led to the conclusion that double-distilled beryllium is of significantly higher purity than single-distilled material, with respect to both soluble and insoluble impurities. Therefore, a reasonably large quantity of double-distilled beryllium was prepared for detailed evaluation of mechanical properties.

In preparing this material, several steps were taken to insure a product of the highest possible purity. First, the distillation apparatus was modified by replacing a dry ice-trichloroethylene cold trap (Ref. 1) with a chevron baffle through which liquid nitrogen is circulated. This arrangement minimized the possibility of contamination of the system with diffusion pump oil. Second, deep etching in HCl after each distillation was employed to eliminate surface contamination by tantalum. Traces of the etchant were removed by immersion in boiling distilled water followed by ultrasonic cleaning in distilled water. Finally, the upper one-third of the single-distilled cones were removed prior to re-distillation. As shown in Figure 5, this insured that only material having a resistance ratio greater than about 180 would be employed for re-distillation.

Three cones of double-distilled material were prepared, yielding approximately 1000 grams. One of the cones was found to contain 12 ppm iron, and also contained traces of the FCC compound ($a = 10.3\text{Å}$). The source of this contamination probably stems from the fact that one of the single distillations performed to provide feed material had been carried to 95% completion. Resistance ratio measurements indicated that most of the iron was probably present in second-phase particles since the resistance ratios for this material are quite high. This is shown in the upper curve of Figure 6. Comparison of the two lines in this curve show the improvement in purity level afforded by the modified procedures described above.

Of the three double-distilled cones, one was set aside for mechanical evaluation in the as-distilled state. The other two cones were subjected to further purification by zone-refining. The cones were cut into strips, 7 inches long by 3/8 inch wide, which were bundled together and zone-melted, using a floating zone technique described elsewhere (Ref. 3). Several rapid zone passes were performed to consolidate the bar, and these were followed by three refining passes at 0.25 inch per hour. A specimen was cut from near the start end of the three-pass bar for measurement of residual resistance. A measurement at 4.2°K was not made, but measurements at 77°K indicated that $R_{300°K}/R_{4.2°K}$ is probably in the range 1400-2000.*

E. Mechanical Property Studies of High-Purity Beryllium

While double-distilled beryllium was being prepared, experiments were carried out to develop improved fabrication procedures for distilled beryllium. It was felt that the initial difficulties encountered in fabricating distilled beryllium were associated with the large grain size of as-distilled and distilled and vacuum-melted material. In order to achieve fine grain size in the

* This specimen was subsequently measured at Bell Laboratories and resistivity ratio of 1540 was obtained.

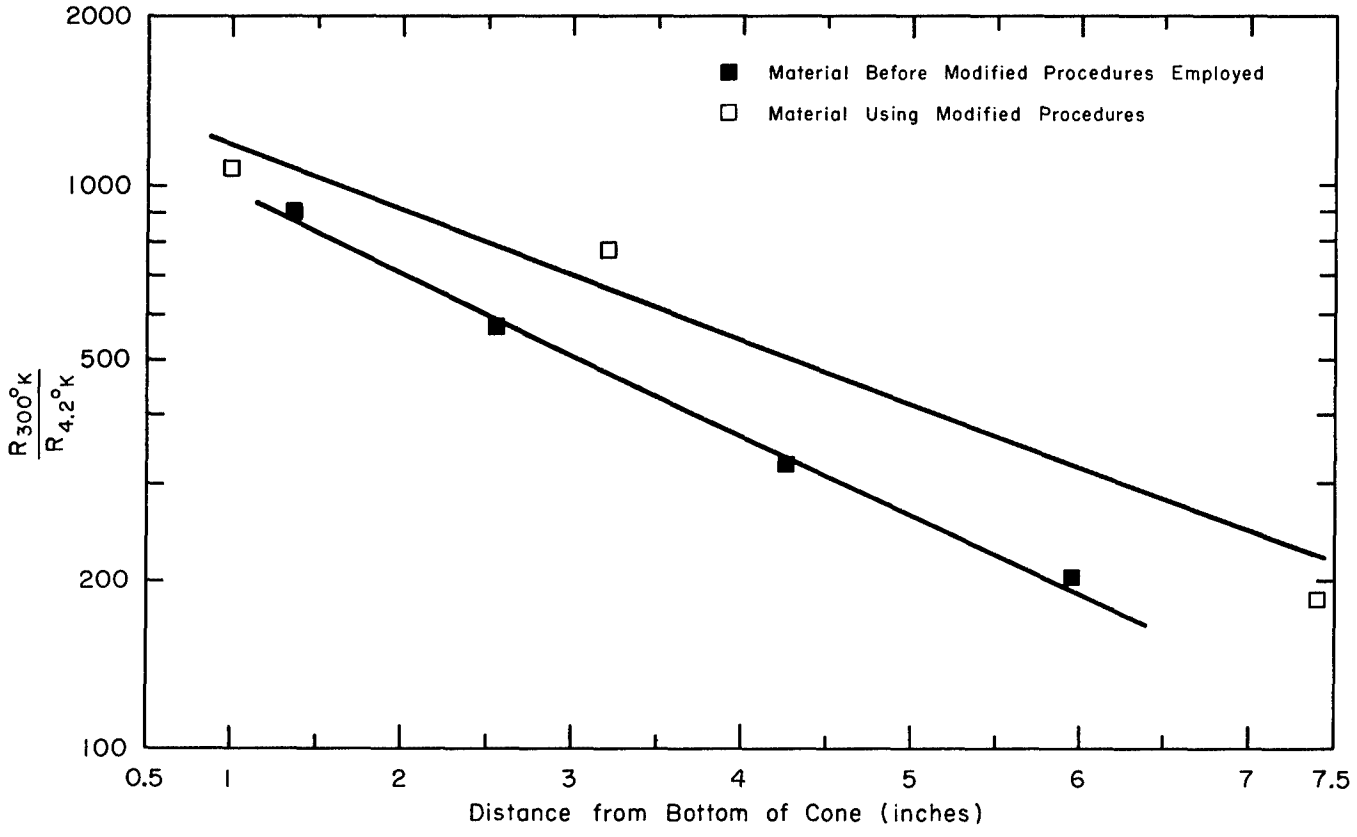


Fig. 6 - Impurity gradient in double-distilled beryllium. Drawing No. RA-2662.

final state, it would be necessary to include a grain-refining procedure before final fabrication. In order to accomplish this, powder metallurgy techniques were employed.

Experiments were conducted on material of several purity grades in order to measure directly the effect of purification on mechanical properties. The following materials were employed:

(1) Brush QMV -200 mesh powder

(2) Vacuum-melted Pechiney CR grade flake

(3) 5-pass zone-refined Pechiney CR grade flake

(4) Pechiney SR grade -110 mesh powder

(5) Single-distilled beryllium

(6) Double-distilled beryllium

Fifty-gram batches of the above materials that were not already in powder form were attritioned in a beryllium mortar with a beryllium pestle, both constructed from Pechiney CR grade beryllium. Previous experience had shown that severe contamination of distilled powder occurs during sieve or classifier sizing operations, so no such sizing of powders was attempted in the present experiments. The average particle size of the powders attritioned in this way was approximately 200 microns, the largest particles approximately 500 microns as measured under the microscope. Chemical analyses of high-purity powders are given in Table 5, which indicates that little contamination occurred, except for a small amount of iron pickup, probably from dust particles in the atmosphere.

Powder from each of the above batches was cold-compacted in a beryllium die, and the compacts were sealed in outgassed steel cans. The billets were extruded into flats at 1650°F; this low extrusion temperature being employed in order to prevent grain growth. The extruded flats had a cross section of 0.75 x 0.075 inch. The reduction ratio in extrusion was approximately 12 to 1.

The extruded flat made from single-distilled powder had an elongated blister over its entire length, and the cross section contained numerous voids. No mechanical test specimens could be obtained from this extrusion. The other extrusions, however, were successful, and were machined into tensile and bend specimens.

As-extruded microstructures are shown in Figures 7 through 11. These photographs exhibit the influence of both initial particle size and purity on the extruded grain size and structure. For example, the Brush QMV extrusion, Figure 7, as a consequence of the low extrusion temperature, had an unusually fine grain size of approximately 6 microns. The Pechiney SR extrusion, Figure 10, with a larger initial particle size, had a grain size of approximately 10 microns. Examination of the longitudinal section of this extrusion, Figure 10b, shows that a small amount of recrystallization has taken place, whereas no such behavior was exhibited by the Brush material. This is probably a consequence

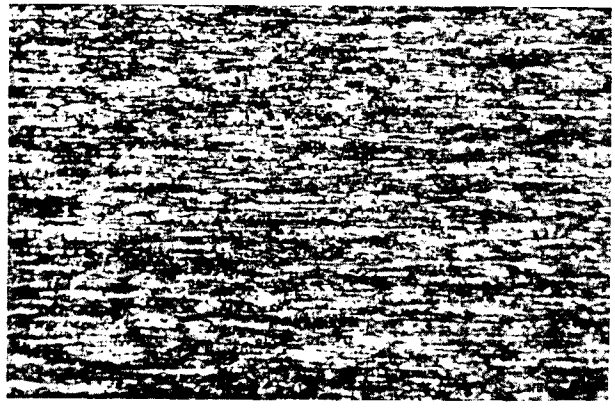
TABLE 5

CHEMICAL ANALYSES OF POWDER ATTRITIONED FROM HIGH-PURITY BERYLLIUM

Material	Impurity Concentration, ppm		
	Fe	Si	Cr
Single Distilled	10-25	25	2
Double Distilled	6-9	13	<1

100X Pd Lt. B-485-3 T

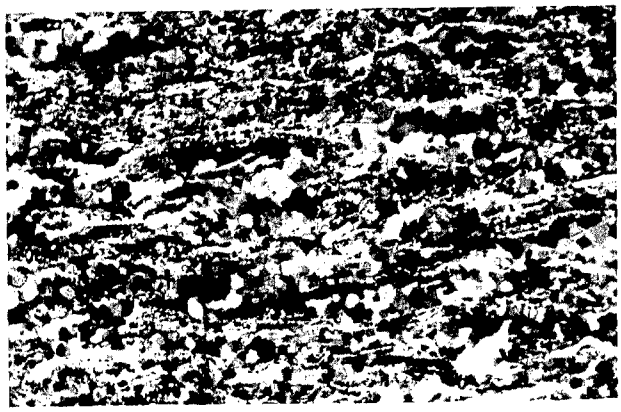
(a) Transverse section



100X Pd Lt. B-485-3 L

(b) Longitudinal section

Fig. 7 - Microstructure of flat extruded from Brush QMV -200 mesh powder.



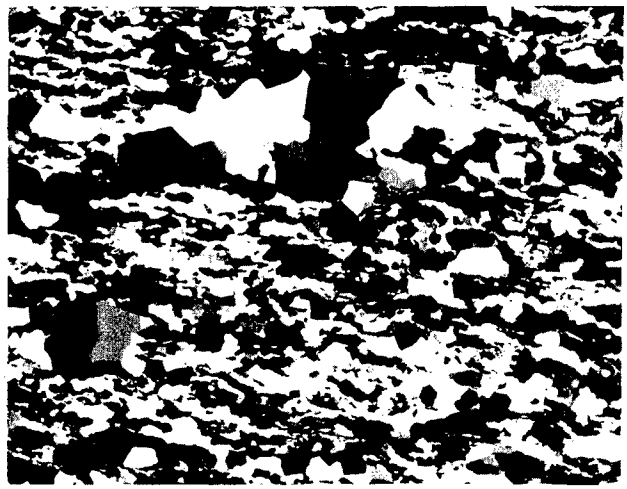
100X Pd Lt. B-485-1 T

(a) Transverse section

100X Pd Lt. B-485-1 L

(b) Longitudinal section

Fig. 8 - Microstructure of flat extruded from vacuum-melted Pechiney CR grade powder.



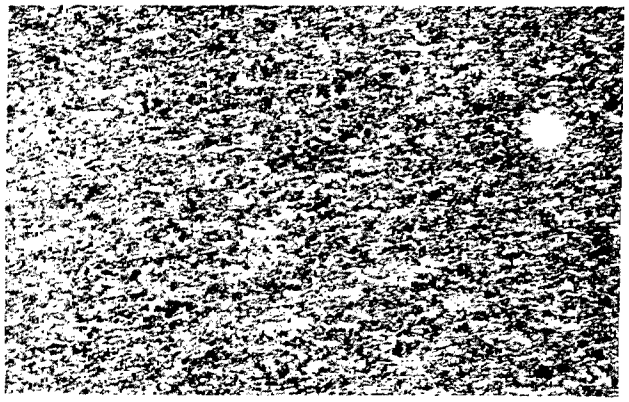
100X Pd Lt. B 487a

(a) Transverse section

100X Pd Lt. B 487b

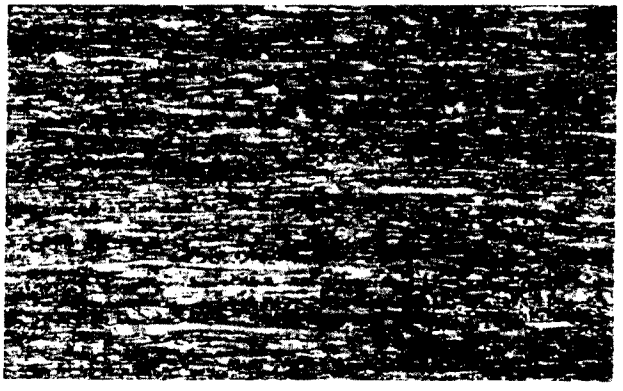
(b) Longitudinal section

Fig. 9 - Microstructure of flat extruded from powder prepared from 5-pass zone-refined Pechiney CR beryllium.



100X Pd Lt. B-485-4 T

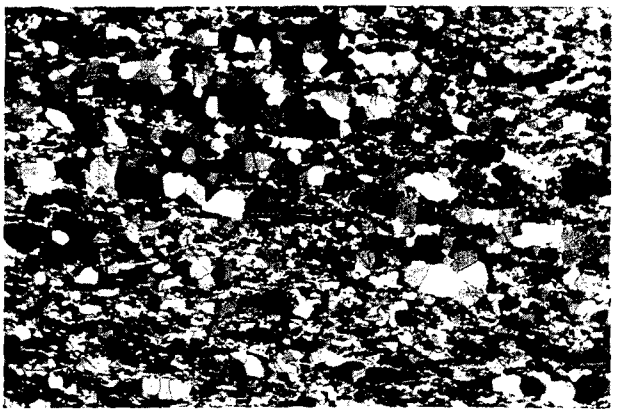
(a) Transverse section



100X Pd Lt. B-485-4 L

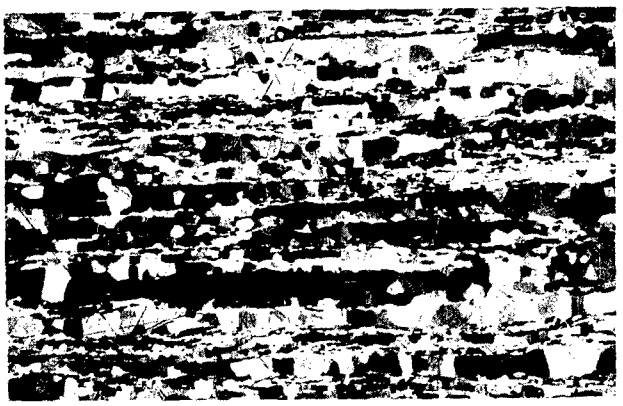
(b) Longitudinal section

Fig. 10 - Microstructure of flat extruded from Pechiney SR -110 mesh powder.



100X Pd Lt. B-485-2 T

(a) Transverse section



100X Pd Lt. B-485-2 L

(b) Longitudinal section

Fig. 11 - Microstructure of flat extruded from double-distilled beryllium powder.

of a change in deformation and recrystallization behavior of beryllium with increasing purity.

The vacuum-melted Pechiney CR material, the double-distilled beryllium, and the zone-refined material, all having larger initial particle sizes, had considerably larger grain sizes after extrusion: 20, 30, and 50 microns, respectively. A purity effect on recrystallization behavior is quite evident. The Pechiney beryllium, Figure 8b, is partially recrystallized, whereas the double-distilled beryllium, Figure 11b, and the zone-refined beryllium, Figure 9b, appear to be completely recrystallized.

Texture measurements were performed on each flat. The technique employed was one originally developed by Shulz (Ref. 11) and modified by Decker et al (Ref. 12). Circular discs were cut from the extruded flats with faces parallel to the major extrusion surface. The discs were all 5/8 inch diameter and 0.050 inch thick. A disc of identical geometry was machined from a hot-pressed block to provide a random standard. Each disc was mounted in a special fixture on a Norelco diffractometer and irradiated with CuK_{α} radiation at 35 kv, 19 ma. The plane of the sample was maintained in a fixed position with respect to the X-ray beam and rotated 360° about the disc axis at a low speed while the diffracted intensity is recorded on a chart. After each rotation, the fixed position was altered by tilting the sample about an axis perpendicular to the incident and diffracted X-ray beams. The specimen was then rotated through 360° at the new tilt angle. In this way, planes lying at any discreet angle with respect to the plane of the extruded flat and in all directions with respect to the extrusion direction could be investigated. Five-degree increments of tilt were employed from 0 to 90° to determine the complete $(11\bar{2}0)$ pole figure. An identical study was made of the hot-pressed random sample. By comparing each extruded sample with a random sample of identical dimensions, all geometrical effects caused by tilting the samples were eliminated.

The results of the texture measurements revealed that the preferred orientation was the same within experimental error in all materials. In each case, there was a concentration of basal planes parallel to the extrusion direction and 40°-50° to the plane of the flat, with the $<10\bar{1}0>$ in the extrusion direction. The commonly observed basal plane inclination in extruded flats is 70° (Ref. 7), but Jacobson and Underwood have also described a 45° orientation (Ref. 8). It might be expected that the extrusion geometry would exert an influence on the texture such that as the width-to-thickness ratio of the flat increases, the texture would approach that of rolled sheet.

Chemical analyses of the extrusions are given in Table 6.

Mechanical properties were evaluated by means of tensile and bend tests. Bend tests were performed on specimens 0.050 inch thick, with various widths up to 0.675 inch. Tests were performed on a three-point bending apparatus. A 0.200-inch radius ram pushed the specimen at a rate of 0.01 inch per minute between 2.400-inch diameter steel rollers with centers 3.00 inches apart. Bend angle at fracture as a function of specimen width for the different materials is shown in Figure 12. The double-distilled material exhibited significantly greater transverse ductility than the other materials tested. The bend angles observed for the widest specimens (50°-70°) are higher than any reported for beryllium of comparable width-to-thickness ratios.

TABLE 6

CHEMICAL ANALYSES OF BERYLLIUM POWDER EXTRUSIONS

Material	Impurity Content, in ppm			
	Fe	Ni	Al	Si
Brush QMV	1115	170	540	240
Vacuum-melted Pechiney CR	225	90	41	32
5-pass zone refined	181	123	11	10
Pechiney SR	66	4	110	50
Double distilled	16	1	20	18

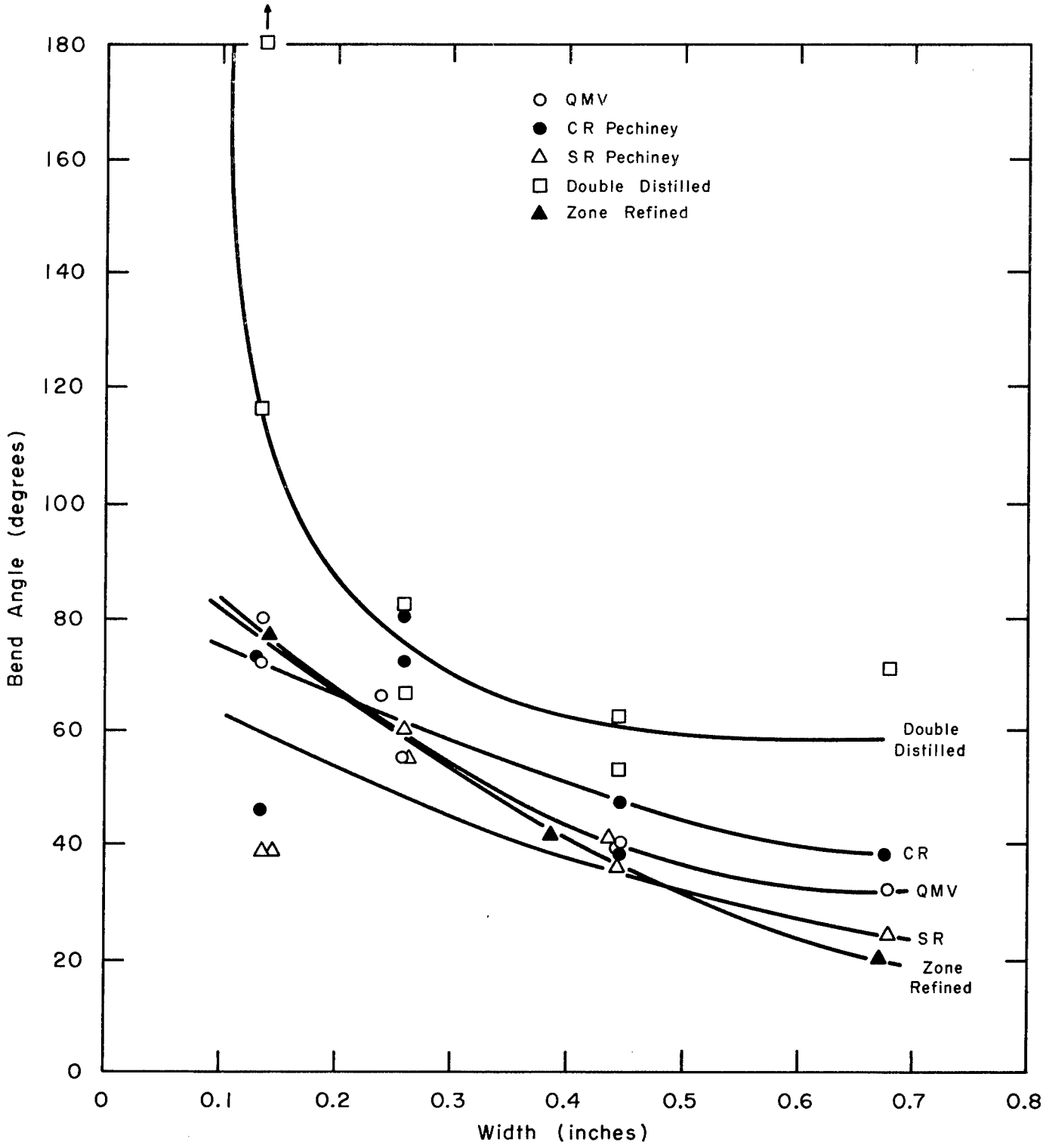


Fig. 12 - Bend angle vs. specimen width.
Drawing No. RA-2485.

Figure 13 presents results of calculations of the tensile strain in the outer fibers of the bend samples. These results are based on radii of curvature measured on the fractured samples. The results are in qualitative agreement with the bend angle - sample width results of Figure 12.

The basal plane inclination in the extruded flats is such that plastic deformation in the sheet thickness direction during bending would be expected to take place predominantly by basal slip. Since single crystal studies (Ref. 2) have shown that basal plane ductility in beryllium is greatly increased by purification, the high transverse ductility in double-distilled beryllium appears to be a direct consequence of purification.

Flat tensile specimens, having reduced section dimensions 1 inch by 1/4 inch by 0.050 inch, were employed. Testing was performed in a 60,000 pound capacity Tinius-Olsen mechanically driven machine, at a strain rate of 0.01 per minute.

Tensile properties are presented in Table 7. Since these tests were performed with the tensile axis parallel to the extrusion direction, deformation by prismatic slip would be expected on the basis of the observed texture. Ductility in single crystals oriented with the $\langle 10\bar{1}0 \rangle$ parallel to the tensile axis has been observed to be relatively unaffected by purification (Ref. 3), so the similarity in tensile elongation between the different materials shown in Table 7 appears reasonable.

The percentage change in yield stress for prismatic slip in a single crystal has also been shown (Ref. 3) to be small (it is estimated that the critical resolved shear stress for prismatic slip in a single crystal made from double-distilled beryllium would be approximately 80% of that in a crystal made from QMV material). Therefore, only a small purity effect on the yield strength would be expected in these experiments. Actually, even this small effect appears to have been marked by differences in grain size. Figure 14 shows that both yield and tensile strengths of the extruded flats appear to follow the familiar $d^{-1/2}$ relationship.

Several conclusions can be drawn from the fabrication and mechanical property studies described above. With regard to the development of fabrication techniques for high-purity beryllium, the powder metallurgy route appears to have distinct advantages over other methods, in that a fine grain size can be produced with only a minor amount of contamination (exclusive of oxygen*). The attritioning operations performed in these experiments were quite crude, and relatively simple modifications to permit environmental control would be expected to reduce contamination even further. The same is true regarding particle size control, which would permit a closer matching of as-fabricated grain size among different starting materials. In order to accomplish these ends, some work was begun to construct a beryllium-lined ball mill for vacuum or inert gas attritioning to standard particle size ranges.

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* It has been implicitly assumed throughout this study that the presence of BeO on the surface of the powder particles produced by attritioning would have little effect on the mechanical properties of the consolidated bodies. It was intended to check this point at a future date by the production and consolidation of powder in an inert atmosphere and comparing the behavior of bodies so produced with those produced in air.

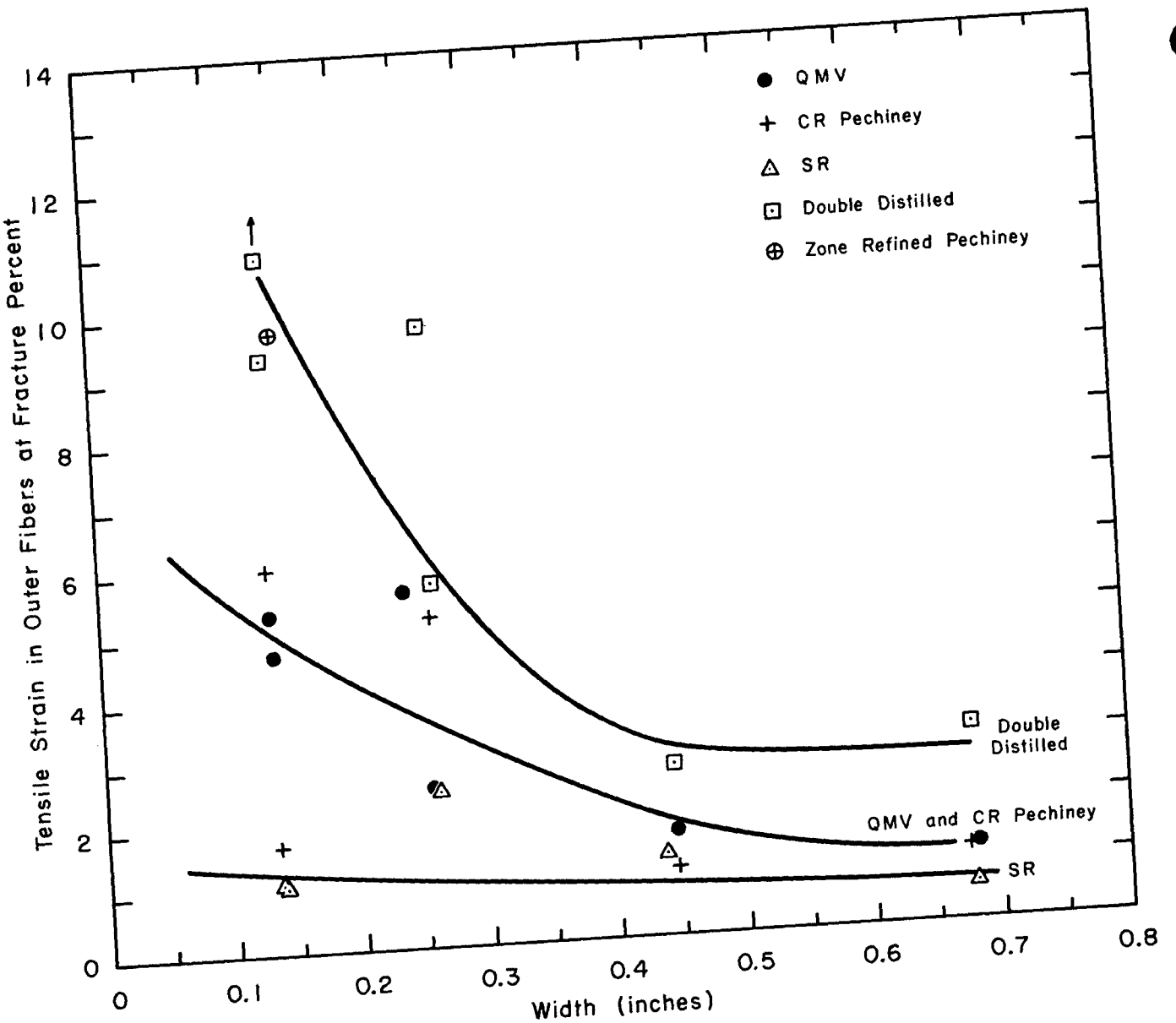

Fig. 13 - Outer fiber tensile strain of fractured bend samples. Drawing No. RA-2663.

TABLE 7

TENSILE PROPERTIES OF BERYLLIUM POWDER EXTRUSIONS

Material	0.2% Offset Yield Strength (psi)	Ultimate Tensile Strength (psi)	Percent Elongation
Brush QMV	71,400	111,000	7.3
Vacuum-melted Pechiney CR	24,000	72,400	9.7
5-pass zone refined	15,000	58,200	7.5
Pechiney SR	61,400	95,600	5.4
Double distilled	22,500	63,700	7.6

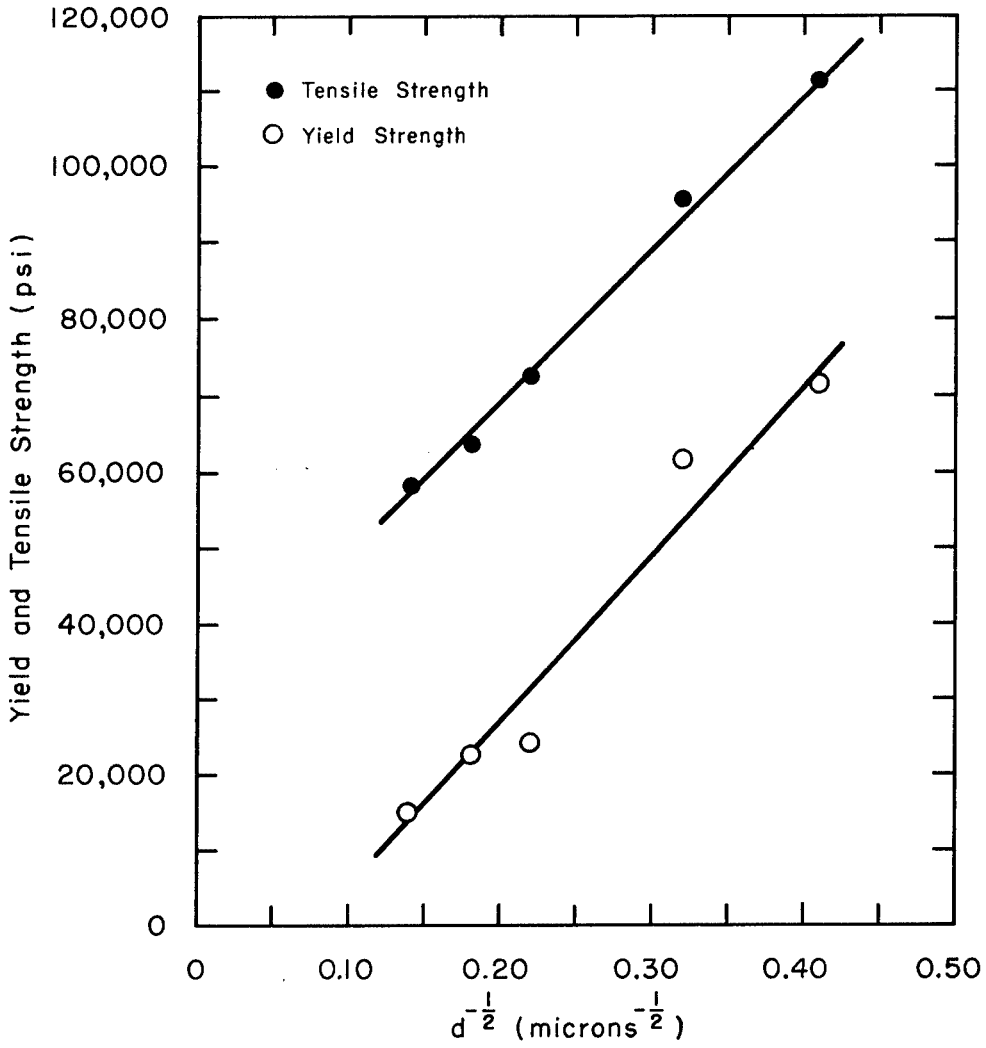

Fig. 14 - Grain size dependence of strength in beryllium powder extrusions. Drawing No. RA-2664.

With regard to the properties of high-purity beryllium, the above studies have shown that transverse ductility is significantly improved by purification. With the discovery that extruded flat texture can probably be controlled by extrusion geometry, it should be possible to obtain tensile samples oriented to favor basal slip, and therefore to demonstrate the effect of purity on mechanical properties in a simple tension test.

F. Summary

1. Studies were undertaken to describe the nature of impurities in beryllium purified by vacuum distillation, to develop procedures for fabricating distilled beryllium to obtain test specimens of high metallurgical quality, and to evaluate the mechanical properties of distilled beryllium.

2. Impurity distribution was studied by chemical analysis, electron microbeam probe analysis, X-ray diffraction, and residual electrical resistance measurements. Distilled beryllium was found to contain only trace amounts of impurities in solid solution, plus a small amount of second-phase constituent containing principally iron and silicon. The impurity phase exists in the form of spherical particles, approximately one micron in diameter. These particles probably limit ductility severely.

3. Double-distilled beryllium appears to be lower in both soluble and insoluble impurities than single-distilled beryllium.

4. Distillation procedures were modified to permit the preparation of double-distilled beryllium of exceptionally high purity. Further purification was obtained by zone-refining of double-distilled beryllium.

5. Fabrication studies indicated that a fine, uniform, recrystallized grain structure of controlled preferred orientation could be obtained without significant contamination by attritioning distilled beryllium to powder and extruding into flats.

6. Double-distilled beryllium fabricated in this way exhibited significantly greater amounts of transverse ductility as measured in bend tests than material of lower purity. The ductility observed in these tests is attributed to basal plane slip and the improvement in ductility with high purity relates directly to the increased capacity for basal slip observed in high purity single crystals.

7. Tensile elongation in the extrusion direction in which slip occurs principally on the prism planes shows little improvement with purification, again in agreement with observations on single crystals.

8. Yield and ultimate strengths in the extrusion direction (prism slip) show the well known linear variation with the reciprocal of the square root of the grain size.

G. Recommendations for Further Work

The findings of this program clearly demonstrate that high purity beryllium of extremely fine grain size and optimum texture will have greater ductility and strength than presently available commercial beryllium. Further work to explore this problem fully should be carried out.

III. PREPARATION AND EVALUATION OF HIGH-PURITY BERYLLIUM SINGLE CRYSTALS GROWN FROM THE MELT

S. H. Gelles*
(Nuclear Metals, Inc., West Concord, Massachusetts)

A. Introduction

Studies of high-purity beryllium single crystals produced by a floating zone refining operation have shown a consistent decrease of the critical resolved shear stress (CRSS) for both basal and prism slip with increasing purity level as measured both by chemical analysis and by the electrical resistivity ratio (resistance at room temperature divided by the resistance at 4.2°K, $R_{RT}/R_{4.2}$) (Refs. 13, 14). In addition, it was found that the ductility when measured on samples oriented for basal plane slip generally increased with increasing purity level.

A large amount of the research work on the mechanical properties of beryllium single crystals was conducted in the early 1950's on material of commercial purity grown from the melt (Refs. 15, 16). It was generally concluded from these early studies that a small amount of slip on the basal plane gave rise to fracture after only a small amount of deformation. The CRSS for slip on the basal plane was reported to be approximately 2000 psi (Ref. 15). The elongation was approximately 2% for crystals with their basal planes oriented 45° to the tensile axis. These results have recently been confirmed by Herman and Spangler (Ref. 2) at The Franklin Institute using the same fabrication and testing conditions on commercially pure beryllium single crystals grown from the melt as were used for crystals grown by the floating zone technique.

A recent Russian study conducted by Garber, Gindin, and Shubin (Ref. 17) on single crystals grown from the melt from distilled metal showed an excessively large CRSS for basal slip - 4400 psi compared to approximately 2000 psi for commercially pure beryllium. The Russian investigators reported a resistance ratio, $R_{298}/R_{4.2°K}$, of 16.7. Based on the relationship delineated by Kaufman et al (Ref. 14) for zone-refined crystals, a CRSS of 920 psi would be expected for a beryllium single crystal having a resistance ratio of 16.7. Although the relationship may not be exactly applicable to the results of Garber et al (Ref. 17), since specific impurities may affect the resistance ratio to varying extents, it is apparent that the values of the CRSS for basal slip determined by Garber et al (Ref. 17) are higher than expected.

In addition, the elongation observed in the Russian work on a crystal with basal plane oriented at 45° to the tensile axis was the same as that observed on commercially pure single crystals similarly oriented. Current feelings on this latter work tend to discard these results as due to bad experimental procedure. A possible explanation is that sufficient damage was introduced into the beryllium during the grinding or mechanical polishing operations to raise

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the CRSS to the high level reported. Herman (Ref. 18) suggests that this behavior may be explained by geometric considerations. The samples shown by the Russian authors were rectangular in nature, estimated to be 2.4 by 1.6 mm from the illustration of fractured samples shown in the paper (Ref. 17). Since the crystals were oriented with the slip direction, $<11\bar{2}0>$, perpendicular to the short dimension of the cross-section, it is reasoned by Herman that excessive constraints inhibiting the rotation of the basal planes during plastic deformation could lead to a higher CRSS for basal slip.

In an effort to delineate differences in mechanical behavior between zone refined crystals and those grown from the melt in BeO crucibles, a small study was initiated to determine the differences in flow characteristics of high purity beryllium single crystals grown by these two techniques. Such differences could result from differences in dislocation, density, and/or distribution arising from differences in the growth conditions or could arise from impurity pick-up from the beryllium oxide crucible or atmosphere. The impurity could be oxygen or carbon or perhaps silicon or aluminum and might be present either distributed as second-phase particles or be dissolved in the beryllium matrix.

It was felt that this type of study could shed some light on the role of impurity and/or substructure on the mechanical properties of beryllium single crystals, as well as providing a check on the unusual Russian results cited above.

B. Experimental Procedure

1. Materials

Single crystal samples were prepared from SR grade Pechiney beryllium flake which had been vacuum melted in a BeO crucible in a vacuum of 10^{-5} mm of Hg and from chunks of singly distilled beryllium prepared at Nuclear Metals (as reported in Section II of this report).

2. Preparation of Single Crystals

Large crystals of the vacuum melted Pechiney SR grade beryllium and of distilled beryllium were prepared by melting the metal in beryllium oxide crucibles in a vacuum of approximately 10^{-6} mm of Hg and directionally solidifying the metal from the bottom up. The equipment used for preparing the large crystals is shown in Figure 15. It consists of a belljar pumped by an oil diffusion pump which is trapped by a liquid nitrogen cooled chevron baffle and is the same system used for producing the high purity distilled beryllium (as reported in Section II of this report). A three-zoned furnace consisting of tantalum wire wound on a beryllium oxide cylinder occupies the center of the belljar and is surrounded by tantalum radiation shielding. The three zones of the furnace are independently controlled so that a temperature gradient (highest at the top and lowest at the bottom) can be maintained during the solidification of the melt. The temperature is monitored by a thermocouple placed at the bottom center of the BeO crucible containing the molten beryllium. Power settings to the three zones had previously been determined in calibration runs so as to produce the desired gradient.

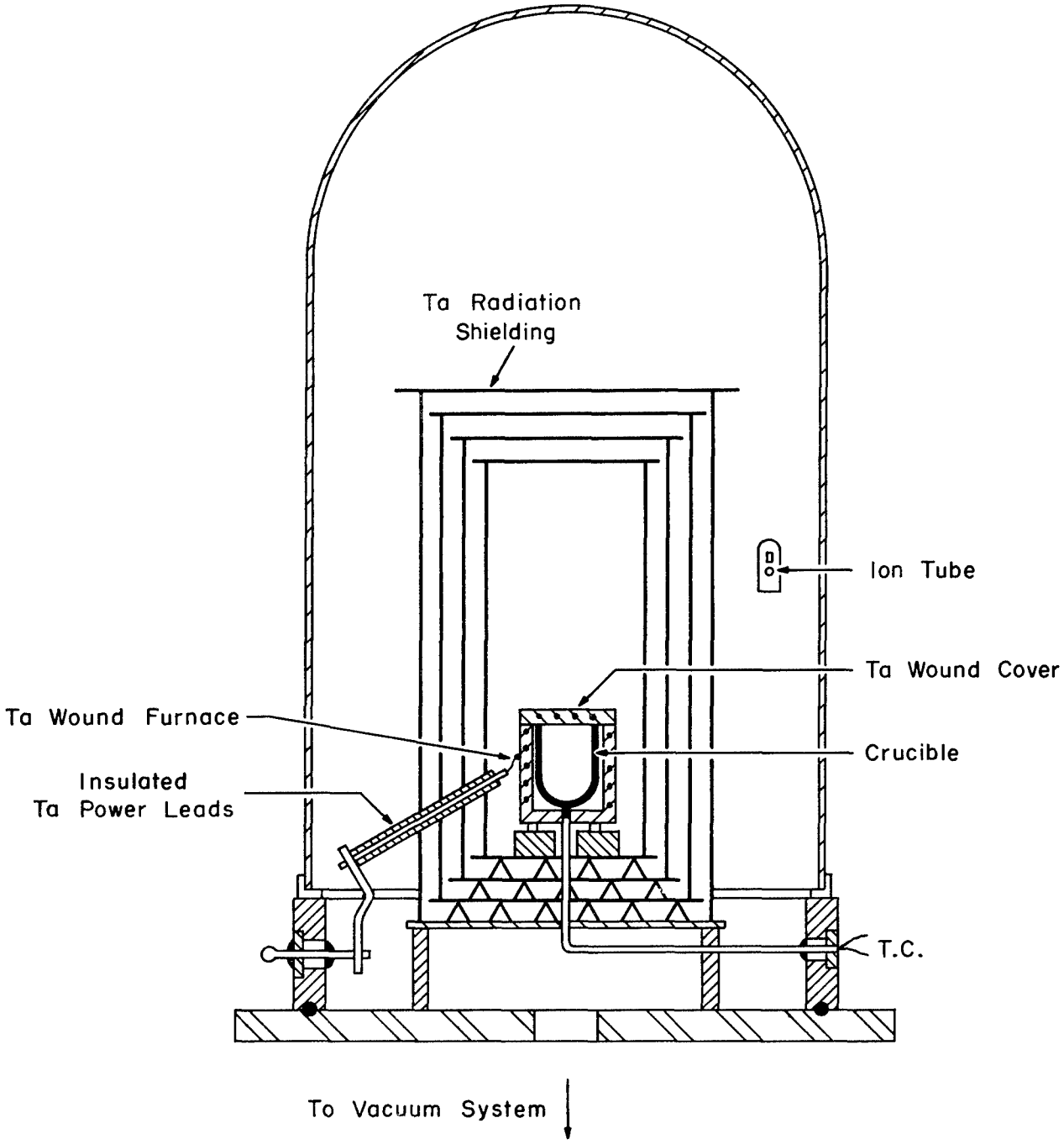

Fig. 15 - Schematic diagram of apparatus used for growing large beryllium single crystals. Drawing No. RA-2682.

In the experiments for producing large crystals of beryllium, the feed material (625 grams for the Pechiney SR grade beryllium and 266 grams for the distilled beryllium) was placed in a beryllium oxide crucible approximately 2-3/4" diameter by 4-1/8" high. The crucible and metal were set in the distillation apparatus and the beryllium was heated above its melting point in a vacuum of approximately 10^{-6} mm of Hg. The metal was allowed to solidify from the bottom up over a period of between 12-1/2 hours (Pechiney SR grade beryllium) to 16-1/4 hours (distilled beryllium).

As may be seen from Figure 16, which is a photograph of the SR casting, large crystals were produced by this technique. This casting had a line of demarcation approximately one-quarter of the way up its height and a blow hole at its side just above this line. This is an indication that the metal did not completely solidify as intended but that the billet solidified from the bottom up to this line and from the top downward to this line. In spite of this, crystals of more than sufficient size for mechanical evaluation were obtained from this billet. There was no line of demarcation in the case of the distilled beryllium as a result of the smaller amount of material charged. However, the crystals of distilled beryllium were smaller than those of the Pechiney SR grade beryllium but still usable for mechanical testing.

3. Preparation of Test Specimens

Single crystal sections were cut from the Pechiney SR grade and distilled beryllium large grain castings with a cooled silicon carbide cut-off wheel. They were then oriented using the Laue back-reflection technique and tensile blanks spark machine trepanned from the single crystals. Tensile samples were turned by spark machining, the electrolytic polishing techniques described by Kaufman et al (Ref. 14). Gauge lengths of one inch and gauge diameters of 0.100 inch were used. The tensile testing procedure using a strain rate of 0.020 inch per minute was identical to that used by Kaufman et al (Ref. 14), and the results on the mechanical behavior are thus directly comparable to the latter work. Two samples, both in an orientation for basal slip, one from the Pechiney SR grade material and the other from the distilled metal, were tensile tested. A third sample was trepanned from the Pechiney SR billet with the basal plane parallel to the trepanning axis. Only the purity level, as measured by resistance ratio, was determined for this last rod.

The resistance ratio was determined by a DC potential drop technique in which the sample is placed in series with a standard resistor. This technique is described in Section II of this report.

C. Results

Table 8 presents the orientation (ϕ_o, λ_o), resistance ratio ($R_{RT}/R_{4.2^oK}$), CRSS for basal slip (τ_o), elongation (ϵ), resolved shear stress at fracture (τ_f), work hardening parameter ($dT/d\gamma$), and resolved shear strain at fracture (γ_f) for the Pechiney SR and distilled metal crystals tested in this program. The resistance ratios measured for the Pechiney SR and distilled

RF 9013

Fig. 16 - Photograph of Pechiney SR grade billet containing large crystals.

TABLE 8

TENSILE PROPERTIES AND RESISTANCE RATIOS OF VACUUM-MELTED SR PECHINEY FLAKE AND DISTILLED BERYLLIUM SINGLE CRYSTALS

Sample No.	ϕ_o*	λ_o**	$R_{RT}/R_{4.2°K}$	τ_o, psi	ϵ, %	τ_f, psi	γ_f, %	$d\tau/d\gamma$, psi
SR-1-1	90	19	98	----	---	----	----	----
SR-2-1	43	53	68	1415	4.4	1694	9.6	1843 (γ = 0.10)
DSC-4-1	55	35	298	923	9.0	1200	18.4	1491 (γ = 0.19)

* ϕ_o Angle between C-axis and Tensile axis in degrees.

** λ_o Angle between Tensile axis and nearest $<11\bar{2}0>$ in degrees.

crystals are of the expected magnitude and should be compared to a resistance ratio ($R_{RT}/R_{4.2°K}$) of approximately 2.5 for commercially pure beryllium. Thus, the crystals listed in this table are the purest (judged from a resistance ratio standpoint) single crystals tested "as grown from the melt."

The values of CRSS for basal slip given in Table 8 are lower than those reported for the commercially pure single crystals grown from the melt (Refs. 2, 15, 16), in contrast to the values reported by the Russian investigators for their distilled metal single crystals grown from the melt. The values in Table 8, however, lie above the solid line representing the values of critical resolved shear stress versus resistance ratio for floating zone refined beryllium (Ref. 14) as may be seen in Figure 17.

The elongations for the high-purity crystals grown from the melt are generally lower than is observed on crystals similarly oriented grown in the floating zone refining process but well above that of commercially pure beryllium grown from the melt (Refs. 2, 15, 16) (2%). The elongations were found to increase with increasing purity.

The work hardening parameters, $(d\tau/d\gamma)$, shown in Table 8 and Figure 18 are higher than zone refined crystals of comparable resistance ratios. Since the Pechiney SR crystal failed before a 20% resolved shear strain was achieved, the value of the work hardening parameter is given for a resolved strain of 9.6%. However, since most of the resolved shear stress versus resolved shear strain curves for beryllium single crystals oriented for basal slip have a constant value of $d\tau/d\gamma$ in this range of strain, it is felt that the comparison between the strain hardening parameters of the crystals grown from the melt and those obtained on zone refined crystals at a resolved strain of 20% is valid.

As may be seen from the resolved shear stress versus resolved shear strain curves for the Pechiney SR and distilled metal single crystals grown from the melt shown in Figure 19, there is a discontinuity observed with these materials at low strains which is not seen with the floating zone refined material.

D. Discussion and Conclusions

The results on the basal flow characteristics of single crystals grown from the melt in beryllium oxide crucibles show that high-purity single crystals grown in this manner have lower values of CRSS and higher ductilities than those of commercially pure beryllium. The CRSS steadily decreases and the ductility steadily increases with increasing purity as measured by the electrical resistance ratio ($R_{RT}/R_{4.2°K}$). This is in contrast to the results reported by Garber, Gindin, and Shubin in which the CRSS was approximately double that observed in commercially pure material by Tuer and Kaufmann (Ref. 15) and Spangler, Herman, and Arndt (Ref. 2). The resistance ratio reported by the Russian investigators ($R_{298°K}/R_{4.2°K}$) is relatively low for distilled beryllium and indicates possible impurity pick-up which could lead to an increased CRSS by a dislocation locking or a dispersion hardening mechanism.

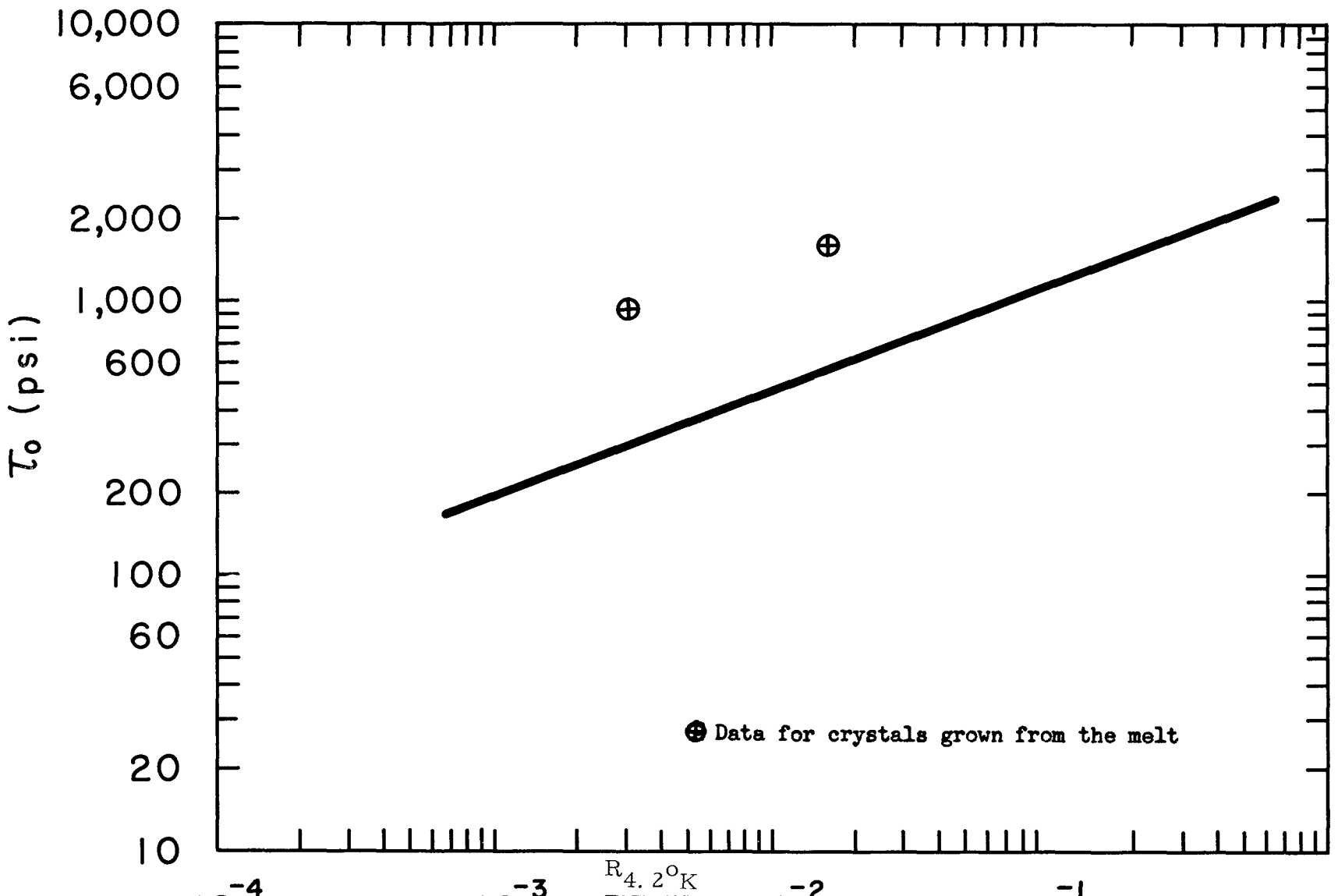

Fig. 17 - Purity dependence of critical resolved shear stress for basal slip. Solid line data of Kaufman et al (Ref. 14). Drawing No. RA-2569.

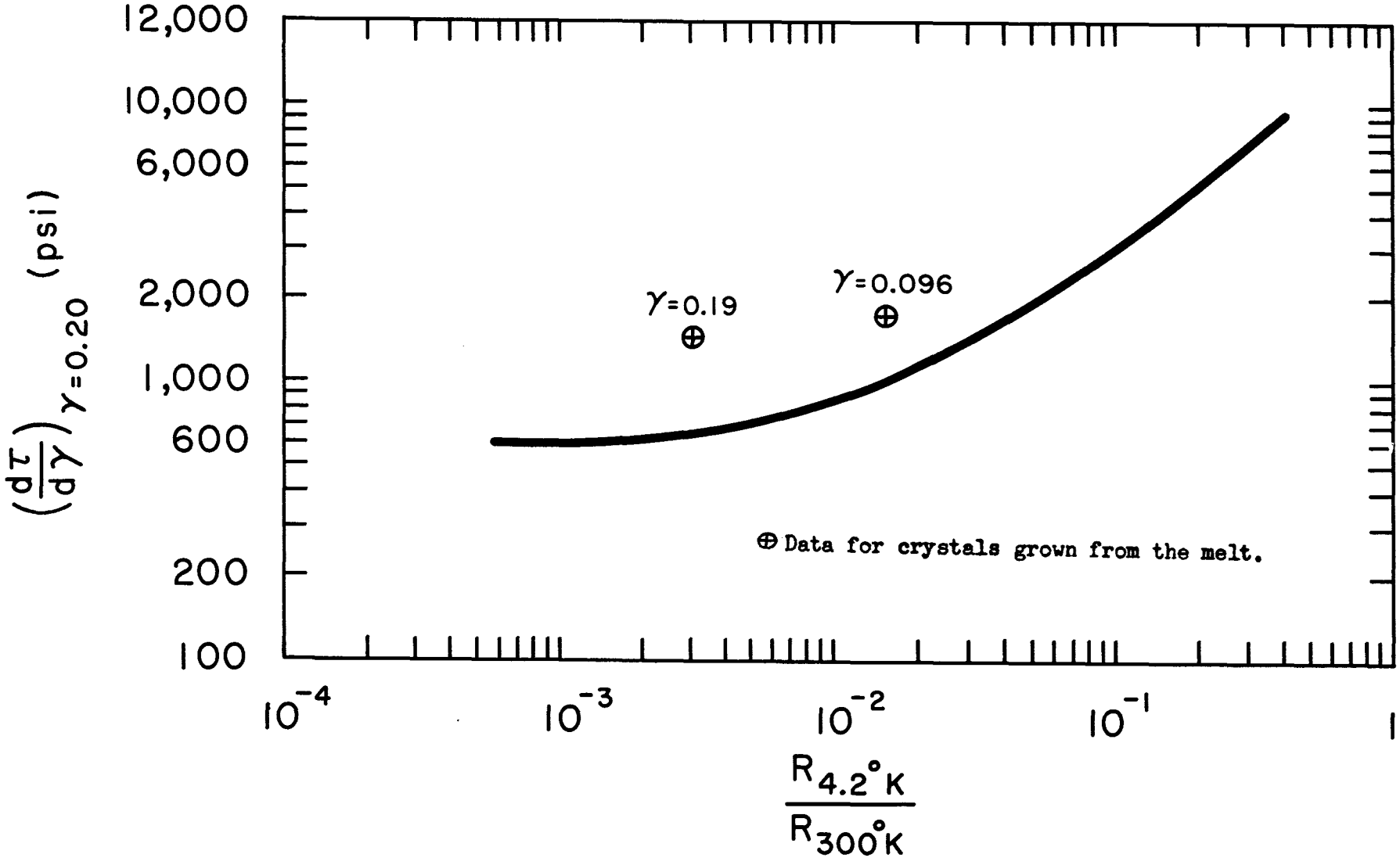

Fig. 18 - Purity dependence of basal work hardening. Solid curve data of Kaufman et al (Ref. 14). Drawing No. RA-2570.

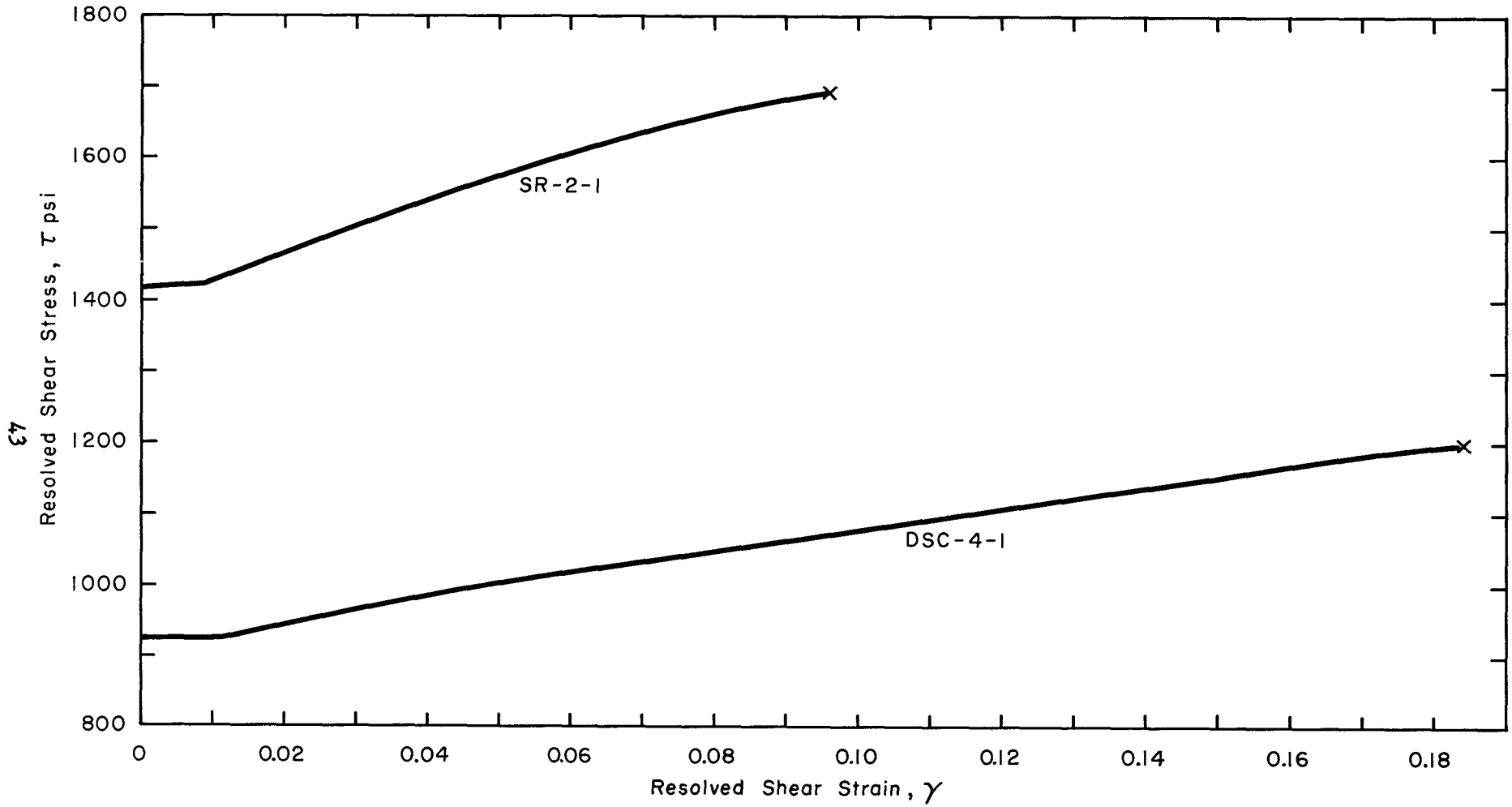

Fig. 19 - Stress-strain relations for beryllium single crystals grown from the melt. Drawing No. RA-2681.

Sample preparation which included mechanical grinding and lapping is another possible source of a raised CRSS or sample geometry may possibly lead to the increase.

The CRSS for basal slip and the work hardening rate, $dT/d\gamma$, on the basal plane were generally greater for the material grown from the melt in a beryllium oxide crucible than for the crystals produced by the zone refining process. This behavior can be rationalized in either of the following ways:

(1) On the basis of selected impurity pick-up, such as oxygen or perhaps carbon, during the growth from the melt process. The impurity could exist in solid solution where it might segregate to dislocation lines causing locking (Ref. 19). The impurity might also collect as a finely dispersed second phase in which form it could cause a raising of the yield strength by the Orowan mechanism (Ref. 20). The presence of a dispersed second phase could lead to premature splitting of bend planes according to a mechanism proposed by Stroh (Ref. 21) and found to be consistent with observed fracture phenomena in beryllium by Spangler, Herman, and Arndt (Ref. 2) and Kaufman et al (Ref. 14).

(2) As a result of differences in dislocation arrangement and density arising from the different methods of crystal growth. Such differences could possibly explain the stress-strain curve discontinuities exhibited by the high purity crystals grown from the melt, and the absence of these in the zone refined crystals. It will be necessary to perform structural studies on the dislocation and impurity phase configuration present in crystals grown from the melt in beryllium oxide crucibles compared to those grown by the floating zone refining process in order to resolve and explain the difference in basal plane slip characteristics.

IV. FINE BERYLLIUM POWDER MADE BY ATTRITIONING

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A. Introduction

Powder metallurgy has already played a considerable role in the development and application of beryllium alloys. Practical beryllium alloys are today produced primarily by vacuum casting of pebble or flake metal into ingots followed by machining, chipping, milling, or similar processes to obtain powders of reasonable purity. Such powders usually have a particle size of -100 or -200 mesh and are consolidated by vacuum sintering or compacting and extrusion.

The powder metallurgy technique provides a means of minimizing anisotropy in extruded or hot pressed sections and fabrication difficulties encountered with cast metal, due to a coarse and orientated grain size, are eliminated. Of

considerable interest in previous work with beryllium powders is the increase in room temperature ductility and strength with decreasing grain size. Associated with this, two general trends have been reported on: the first, that an increase in beryllium oxide content as a result of a finer powder size stabilizes the grain size by limiting grain growth; the second, that the degree of preferred crystallographic orientation decreases with increasing beryllium oxide content, thus resulting in more isotropic structures.

The primary objective of this program was to prepare fine powder in the 1 to 5 micron particle size range that could be consolidated into a fine grained body. Oxide additions to this powder or oxide formation due to surface oxidation of the powder could then define the effect of oxide on the texture and mechanical properties of such a composite. The variables of importance were particle size and contaminant levels in beryllium powder prepared by attirition grinding, a technique capable of producing sub-micron size metal powders described below.

B. Materials

Two sources of beryllium powder for attrition grinding were utilized during the course of this program. They were nominal minus 200 mesh Brush QMV beryllium powder and nominal minus 110 mesh Pechiney CR beryllium powder. The chemical analyses of these powders as supplied by the manufacturer are shown in Table 9. The powders will be referred to as Brush and Pechiney powders, respectively.

C. Equipment

1. Inert Atmosphere Dry Boxes

Two dry boxes were utilized in conjunction with a small and large attritor described below. Both boxes were capable of being evacuated to a pressure of one micron before filling with argon that was passed through a drying column containing molecular sieves and a cold trap. The molecular sieves are dehydrated alkali alumino-silicates and are commercially available at 1/16" pellets from the Linde Company. A standard for operation in the large dry box with the large attritor was the burning of an exposed tungsten filament of a 150-watt bulb for a minimum of five minutes. All processing of powders, including grinding, drying, sampling, and packaging, was conducted within the dry box. During those times when the operator was not working with the box, a positive pressure of 0.5 psi argon was maintained.

2. Attritor Grinding Units

An attritor consists of a stationary, water-cooled tank into which the powder to be ground, a ball charge, and a liquid media are placed. The total charge is kept in motion by the rotation of a spiked shaft. The attritor, supplied by the Union Process Company, is schematically illustrated in Figure 20. Table 10 indicates the pertinent data relative to the charging of the small and large attritor which were incorporated into a small or large dry box, respectively. All grinding was conducted with methyl alcohol as the grinding fluid.

TABLE 9

SUPPLIERS' ANALYSES OF BERYLLIUM POWDERS

Element	Brush (%)	Pechiney (%)
BeO	0.8	1.0
Fe	0.050	0.048
Al	0.030	0.010
Si	<0.020	<0.0055
Ni	<0.020	0.010
Cu	<0.015	0.0040
Cr	<0.010	---
Mg	<0.030	0.0011
Mn	<0.010	0.0017
Ca	<0.010	<0.0455
B	0.00008	<0.0002
C	0.07	0.045

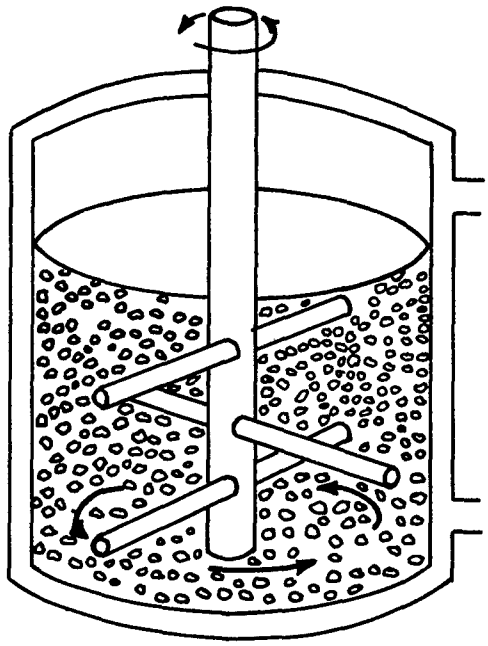

Fig. 20 - Schematic diagram of attritor assembly showing position of spiked shaft relative to fluid and ball charge within a water-cooled tank.

TABLE 10

ATTRITOR CHARGING DATA

	Small Attritor	Large Attritor (Stainless)	Large Attritor (Beryllium)
Capacity (cc)	400	5,000	2,700
Ball Charge (gm)	1,500	15,000	2,500
Liquid Charge (cc)	150	1,500	1,400
Powder Charge (gm)	150	350-400	100
Speed (rpm)	250-360	250-300	250-300

The stationary tank, balls, and spiked shaft used in the small and large attritors were constructed of 304 stainless steel. Subsequent difficulties due to contamination necessitated the use of beryllium bead as the ball charge and a beryllium tube insert and bottom plate within the tank of the large attritor. The charging data for the large attritor with these beryllium components is also included in Table 10. The stainless steel balls were 3/16" diameter and the beryllium balls were beryllium bead sized to minus 1/4" - plus 1/8". The supplier's analysis of the magnesium reduced bead indicated 98.5 percent beryllium and the attritor lining was machined from hot pressed QMV beryllium.

D. Grinding Results

1. Small Attritor

The first grinding run was conducted with Brush beryllium powder and methyl alcohol as the grinding fluid. The total time of grinding was 12 hours with samples for particle size and chemical analysis taken by pipetting from the attritor tank. The particle size was determined by metallographic techniques, discussed in paragraph E below, and the results are included in Table 11.

The analysis procedure for oxygen, determined at Nuclear Metals, Inc., required the beryllium in solid rather than powder form. Sample pellets were prepared in a modified mounting press by pressing at room temperature and 70,000 psi. Beryllium powder after 2 and 12 hours grinding was pressed into pellets of 84% density approximately 6 mm diameter. The pellets were vacuum degassed at 300°F to remove any volatiles from the grinding process. The indicated oxygen contents are shown in Table 12.

In addition to oxygen analysis, powder samples were prepared for iron and chromium analysis. The results, shown in Table 12, indicate intolerable amounts of iron and chromium in the ground powder. The approximate 4 to 1 ratio of iron to chromium indicated the source of contamination to be the stainless steel components and balls of the attritor.

Although the source of contamination was due to the components of the attritor, previous work in the Laboratory had indicated 1.13 percent iron when grinding Pechiney beryllium in a large attritor. With the larger attritor, an increased grinding efficiency had been noted (e.g., less grinding time to achieve a particular size). It was therefore expected that the increased grinding efficiency would reduce grinding time and therefore iron contamination.

2. Large Attritor

The first experiment in the large stainless attritor utilized methyl alcohol and Brush powder. After approximately one hour of grinding, water necessary for the cooling of the attritor tank was accidentally stopped and the heat generated by the grinding action increased the temperature and caused evaporation of the alcohol leaving a dried powder. The particle size and iron content are indicated in Tables 11 and 12. The evaporation of the alcohol during grinding precluded any valid comparison with other grinding studies.

TABLE 11

PARTICLE SIZE OF BERYLLIUM POWDERS (MICRONS)

Grinding Time (Hours)	Largest Observed Particle	Calculated Average Size	Fisher Average Size
	Brush Powder in Small Attritor		
0	160	13.5	12.0
2	25	5.6	--
12	15	2.8	--
	Brush Powder in Large Stainless Attritor*		
0	160	13.5	12.0
1	35	--	--
1.5	25	--	1.0
	Brush Powder in Large Stainless Attritor		
0	160	13.5	12.0
0.5	40	--	4.1
1	40	--	3.6
	Pechiney Powder in Large Stainless Attritor		
0	30	6.0	10.4
1	25	--	3.9
2	15	--	3.1
3	15	--	2.7
4	10	3.1	2.4
	Pechiney Powder in Large Beryllium Attritor		
0	30	6.0	10.4
0.5	10	1.8	--
1.0	9	1.6	--
1.5	7	1.4	--
2.0	7	1.9	--
	Brush Powder in Large Beryllium Attritor		
0	160	13.5	12.0
0.5	20	--	--
1.0	17	--	--
1.5	10	--	--
2.0	7	--	--

* After approximately one hour of grinding, water necessary for cooling of the attritor tank was accidentally stopped and the generated heat caused evaporation of alcohol, leaving a dried powder.

TABLE 12

CHEMICAL ANALYSES OF GROUND BERYLLIUM POWDERS

Grinding Time (Hours)	% Chromium	% Iron	% BeO
	Brush Powder in Small Attritor		
0	0.01	0.05	0.8
2	--	2.46	2.5
4	1.62	6.25	--
6	--	8.85	--
8	2.84	10.75	--
10	--	12.35	--
12	3.40	13.05	10.8
	Brush Powder in Large Stainless Attritor*		
0	0.01	0.05	0.8
1.5	--	0.27	8.0
	Pechiney Powder in Large Stainless Attritor		
0	--	0.048	1.0
1	--	1.43	--
2	--	2.06	--
3	--	2.80	--
4	--	3.51	--

* After approximately one hour of grinding, water necessary for cooling of the attritor tank was accidentally stopped and the generated heat caused evaporation of alcohol, leaving a dried powder.

A subsequent experiment utilizing Brush powder and methyl alcohol indicated an average particle size of 3.6 microns after only one hour of grinding. This size was determined with the Fisher Sub-Sieve Analyzer and indicates significant increase in grinding efficiency in comparison to grinding in the small attritor. No chemical analysis was conducted with this batch of powder.

Pechiney powder was also ground in the stainless attritor with methyl alcohol as the grinding fluid. The particle size and iron contents for powder ground up to 4 hours are shown in Tables 11 and 12. Comparisons of these data with the results indicated for the small attritor indicate that grinding time was materially reduced with the iron contamination seemingly related to time rather than beryllium particle size. It is also to be noted that continued grinding after the first measured time interval reduces the particle size only slightly while the iron content increases appreciably.

The various grinding conditions utilized to this point had presented no difficulty toward obtaining 1 to 5 micron powder. However, in all cases, the iron content was too great. A beryllium insert and bottom plate were prepared, as described above, in addition to beryllium bead substitution for the stainless balls and attritor tank. Unfortunately, later experiments with the beryllium attritor were not checked for iron or beryllium oxide content.

The particle sizes resulting from grinding Brush and Pechiney powders in methyl alcohol and the large beryllium attritor are shown in Table 11. Comparisons with the particle size achieved in the stainless attritor indicated slightly increased grinding efficiency.

Approximately 120 grams of ground Pechiney powder (largest observed particle = 7μ) and 20 grams of ground Brush powder (largest observed particle = 7μ) were prepared in the beryllium attritor with methyl alcohol as the grinding fluid. These powders were then vacuum treated at 300°F to remove the alcohol before shipment to the Air Force Materials Laboratory for disposition.

E. Particle Size Measurement

The particle sizes reported were measured by metallographic techniques and with a Fisher Sub-Sieve Analyzer, when sufficient material was available. The Fisher Sub-Sieve Analyzer employs the air-permeability method for measuring average particle size and the value of the average particle diameter obtained is numerically equal to six times the total volume of the sample divided by the total surface of all the particles in the sample, regardless of particle shape or size distribution. Fisher size measurements of the as-received Brush and Pechiney powders indicated 12.0 and 10.4 microns, respectively. This indicates that the Pechiney powder, on the average, is finer than the Brush powder and is contrary to the stated mesh sizes, minus 200 and minus 110 mesh. A series of powder photographs was taken of each type of powder.

Random areas of each photograph were analyzed with respect to the distribution of sizes present in each powder. Over 1,000 particles of each powder type were measured. Agglomerates were treated as single particles. The Pechiney powder did not indicate any particles or agglomerates coarser than

30 microns, whereas the Brush powder had particles or agglomerates as coarse as 160 microns. Figure 21 indicates the cumulative distribution of particles finer than the indicated sizes present in each type of powder. An overall average particle size was calculated in each case from the distribution data. This calculated average was 6.0 microns for the Pechiney powder and 13.5 microns for the Brush powder. Although the specific values may be questionable due to the size of the sample, the values correlate well with the Fisher measurement in indicating that the Pechiney powder has a smaller average particle size than the Brush powder. Therefore, it was felt that the average particle size as measured by the Fisher technique was a more representative value than screen sizes.

Metallographic size measurements were reported by noting the largest observed particle or agglomerate. When a calculated average particle size measurement was made, a minimum of 1,000 particles was counted and the average calculated from the distribution data.

F. Conclusions

Beryllium powder of 1 to 5 micron particle size can be prepared by relatively short time attrition grinding in either a stainless steel or beryllium attritor. However, the iron content resulting from grinding with stainless steel components is too high for consideration of producing ductile beryllium alloys.

It is suggested that additional powder be prepared by attrition grinding in the beryllium mill and analyzed as to its iron and beryllium oxide content. If the iron content is low, the powder should then be consolidated to investigate the effect of fine grained beryllium stabilized with beryllium oxide leading to more isotropic properties in beryllium alloys.

V. PREPARATION OF ULTRA-FINE BERYLLIUM POWDER

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A. Abstract

A program was instituted to produce ultra-fine beryllium powder in the 0.3 - 0.03μ particle size range. Equipment was installed and operated to produce beryllium powder. Initial evaluation of powder indicated that production techniques and feed materials should be improved to up-grade the final product.

Recommendations for continuing development are outlined.

B. Introduction

The object of this program was to investigate the variables associated with the production of ultra-fine beryllium powder of controlled oxide content in

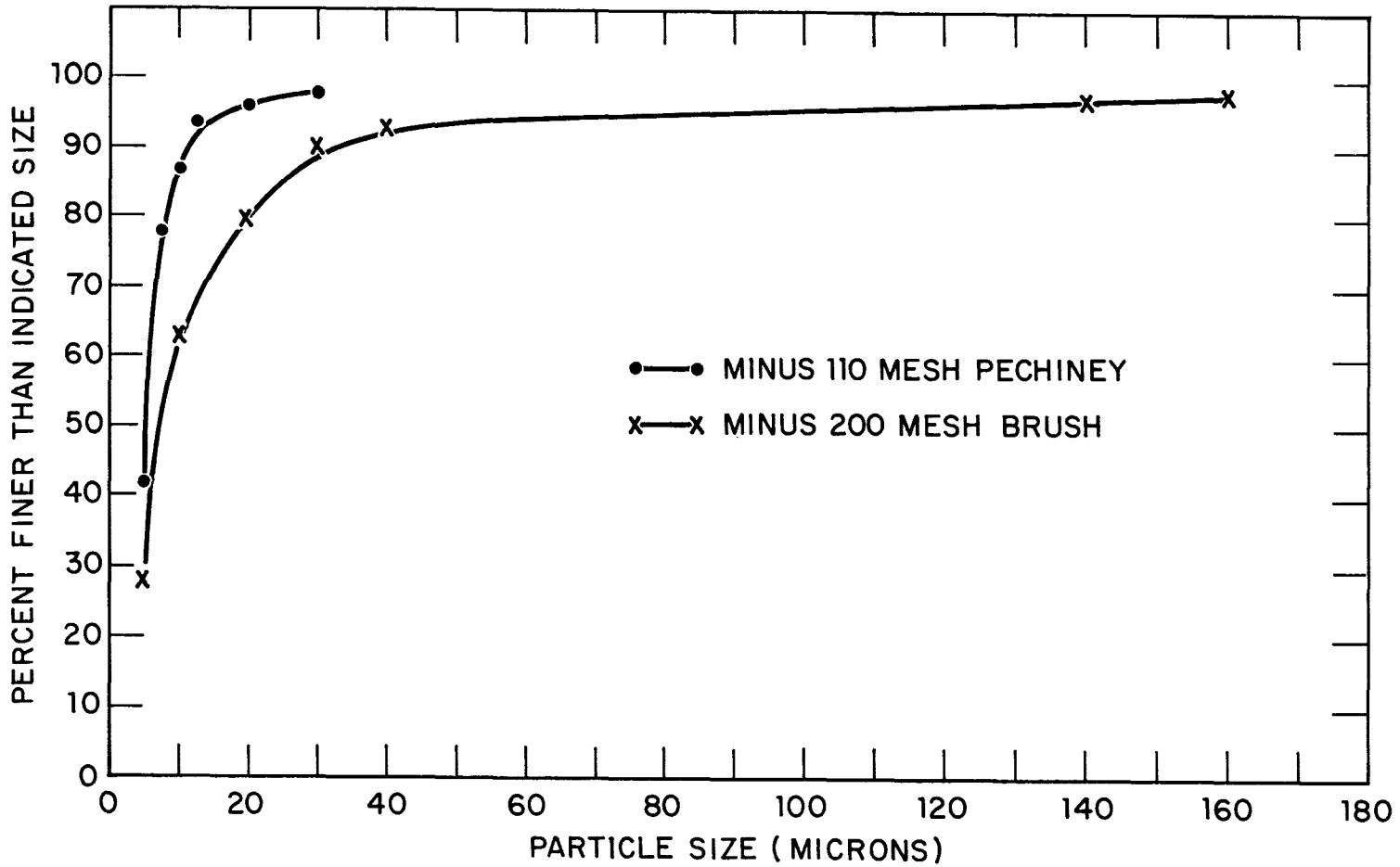

Fig. 21 - Cumulative distribution of beryllium powders

the 0.1 μ - 0.03 μ particle size range, and to prepare samples of ultra-fine beryllium powder for evaluation by Nuclear Metals, Inc. This further evaluation was to include cold compacting and hot pressing, examination of the compacted and pressed material for determination of grain size, chemical analysis of the pressings and of the original powder, and X-ray and microscopic examination of the crystal structure of the finished material.

National Research Corporation has been engaged in the pilot production and research of ultra-fine metal powders. The process for producing ultra-fine metal powders, developed by NRC, is based upon the condensation of metal vapor in an inert gas at reduced pressure. This permits the production of individual or spherical particles in the sub-micron range to be formed in free space. In operation, the vapor evaporates from a source of hot metal, condenses in space, and is collected on the walls of a cooled rotating drum. The powder is removed from the walls of the rotating drum by brushes and falls into a collecting vessel located below the drum assembly. Because of the physiological problems associated with the production of ultra-fine beryllium powder, a new facility was provided by NRC to isolate the work area and prevent contamination of the building and outside work zones.

C. Description of Powder Production Facility

The entire beryllium production facility was housed within a large steel tank, 10 feet in diameter by 15 feet high. The use of this tank enabled the area to remain completely free of beryllium powder which could endanger persons working in the immediate area. Figure 22 shows the tank prior to installation of the equipment. The steel tank was modified to permit access by personnel and to admit the evaporation and powder handling facilities. The 4 foot diameter by 4 foot high cylindrical evaporator with a conical bottom was installed in the large tank and connected to this was a dry box assembly to permit handling of the beryllium powder in a completely inert atmosphere once it had been produced in the evaporator. Materials were loaded into this dry box and the system evacuated and flooded with high purity argon. Glove ports on both the evaporator and dry box permitted operations within these chambers when the pressure was at or near atmospheric. Figures 23 and 24 show the evaporator and dry box assembly within the large tank clean room facility. The conical bottom of the evaporator is removable to permit access to the general evaporator components for modification and cleaning. The vacuum system which was used to reduce the pressure in the evaporator was vented through the air ventilation system. Figure 25 is a line drawing of the system.

Air sampling was conducted during several periods while powder was being produced and transferred to insure that operations were being carried out as planned and that no hazardous quantities of beryllium powder were permitted to escape into the general work area or to endanger those working in the clean room. In addition, air monitors were operated during the time that the system was functioning so as to determine the quantities of airborne beryllium within the tank room, outside of the tank, and in the discharge stream vented to the atmosphere.

D. Operation and Collection of Powder

The evaporator and dry box were operated using aluminum as the first material to be produced as ultra-fine powder. This enabled all personnel engaged

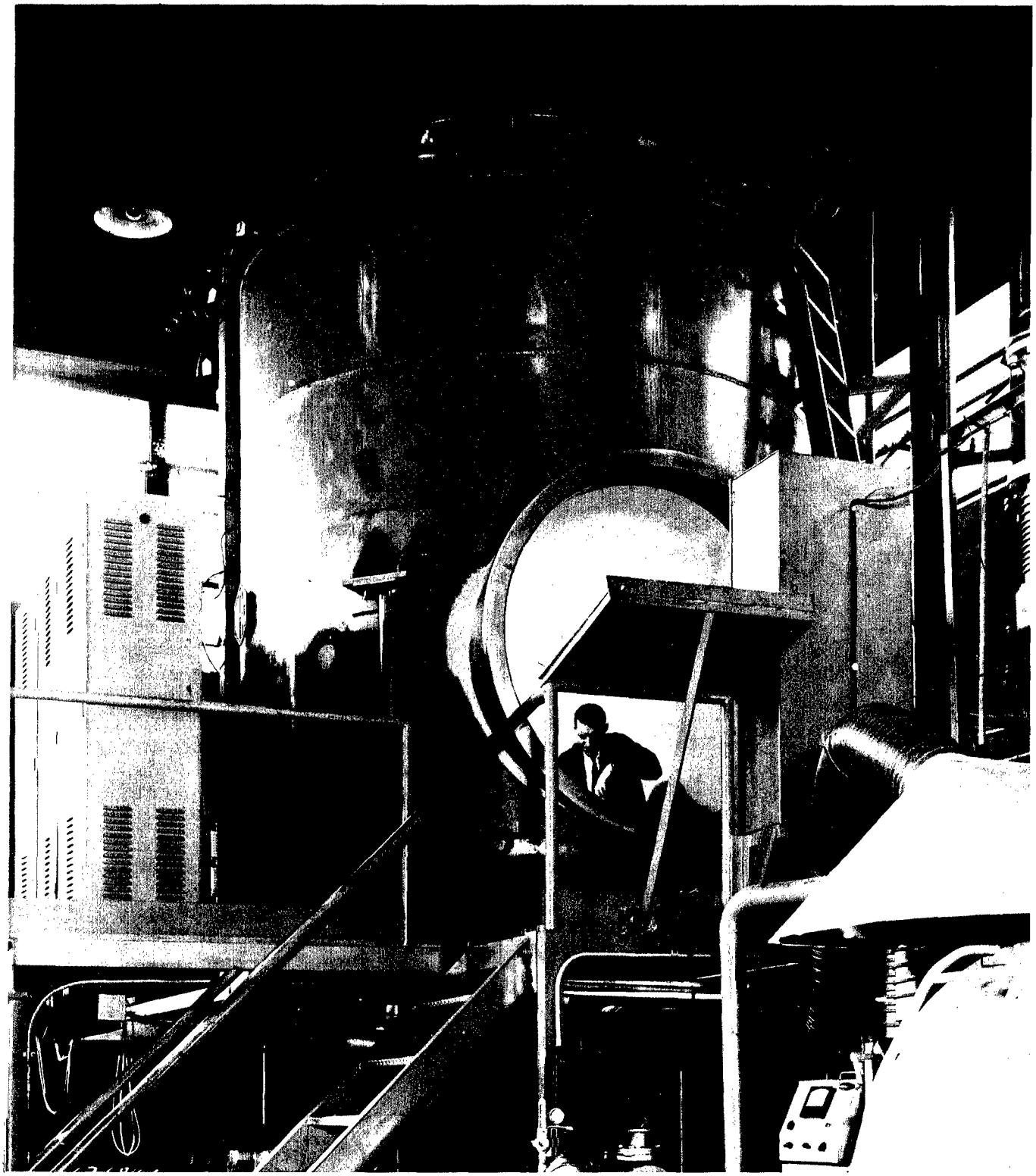

Fig. 22 - View of tank showing modified access port.

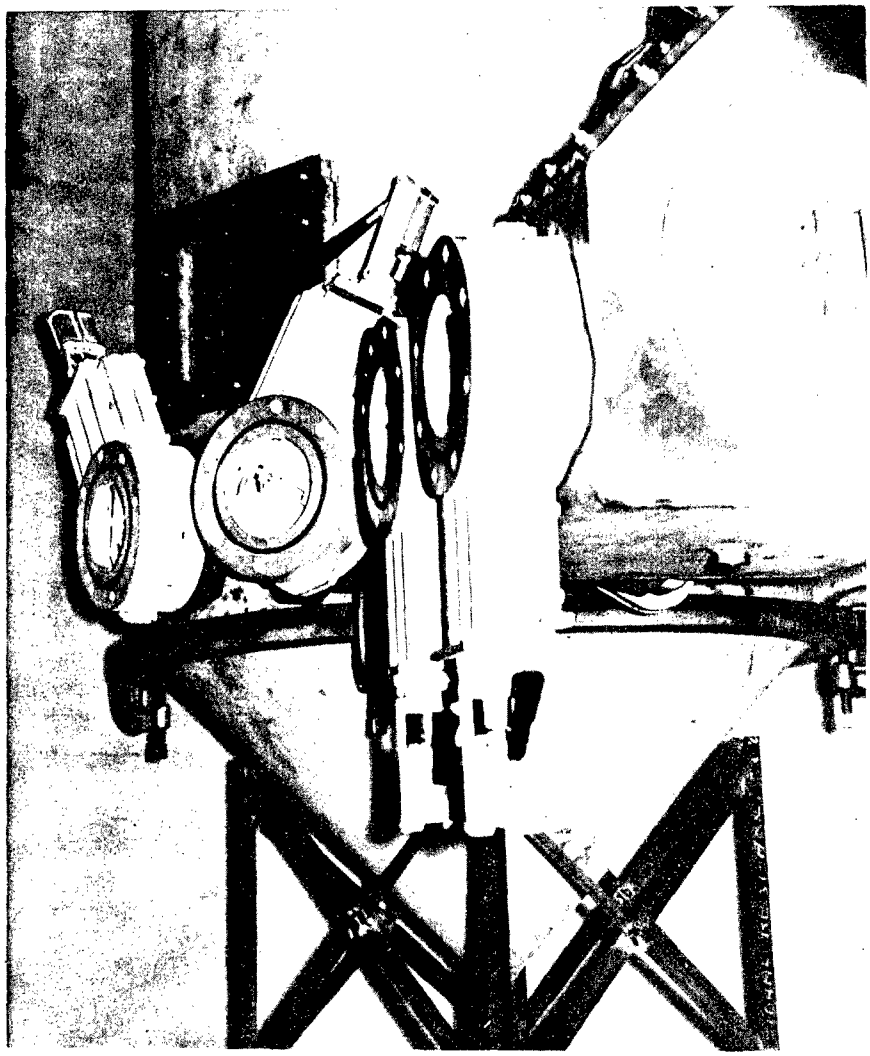

Fig. 23 - View of evaporator and dry box showing glove port valves.

Fig. 24 - View of evaporator and dry box assembly with air ventilating hood over glove ports.

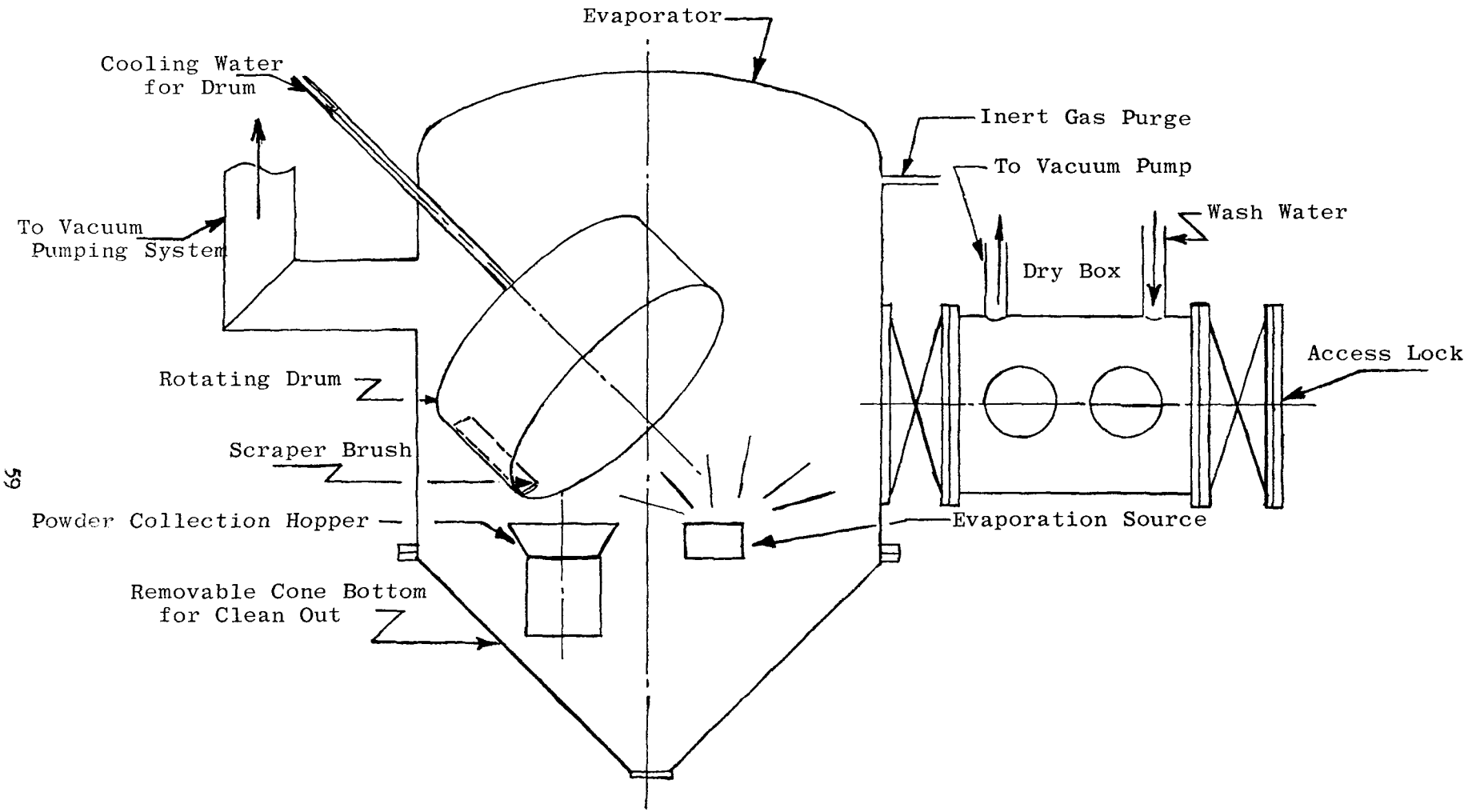

Fig. 25 - Ultra-fine beryllium powder evaporator assembly.

in the program to familiarize themselves with the handling and operating procedures to be used when working with beryllium, without the actual hazards of beryllium. Several highly successful runs in producing aluminum powder were carried out and all phases of the procedure were evaluated. All personnel who were to work with the system were present during at least one set of operations so that each would become familiar with the procedure which was to be followed. At the conclusion of the aluminum powder runs, the tank and dry box facilities were cleaned chemically and wiped down to preclude the contamination of the beryllium powder by the aluminum.

E. Production of Beryllium Powder

Evaporation crucibles for the production of beryllium powder were prefired in a separate furnace to drive off any of the volatile materials present in the carbon and to set the boron nitride coating which had been applied previously. This procedure permitted more rapid start-up for evaporation of the beryllium powder facility since it was not necessary to outgas these crucibles a second time. The outgassing is primarily caused by the volatiles left in the crucible after manufacture and the moisture and gaseous materials absorbed during shipment and handling.

The supply of crucibles which had been prefired was loaded in the dry box assembly together with sufficient vacuum melted beryllium pebble for the initial group of evaporation runs. The beryllium melt stock was preweighed to approximately 150 gram lots; these were packed in individual polyethylene bags so that they would be charged to the prefired crucibles as needed. The crucibles and beryllium were installed in the induction coil in the evaporator and the system evaporated below 1 μ and the leak rate determined. When the leak rate was satisfactory (less than 1 μ per minute), the power was applied to the crucible and the beryllium melted. As soon as the evaporation temperature was reached, argon gas was admitted to the evaporation chamber to the desired pressure, generally between 100 μ and 300 μ. This was the pressure range which had proved most effective to the production of aluminum and it was felt that it would provide a base line in which to initiate the experiments with the beryllium powder. The power was then increased to permit rapid evaporation of the beryllium which occurred at approximately 1450°C as determined optically. Condensation of the beryllium powder in the space adjacent to the rotating drum occurred and the collection of the powder in the hopper below the drum was initiated. The evaporation cycle was carried on for approximately 20-60 minutes, depending upon the life of the crucibles. In some instances, the side reaction of the beryllium with the crucible formed beryllium carbide which, after a period of time, prevented the evaporation of the metallic beryllium by forming a solid non-volatile phase within the crucible. In most cases, it was this reaction which ultimately caused the termination of the run and resulted in the limitation of the production of the beryllium powder.

At the completion of each run, the powder in the collection hopper was removed from the evaporator and transferred to the dry box. The dry box was then brought to atmospheric pressure with argon gas and the powder transferred from the receiving hopper to pint sized glass jars. These jars were immediately sealed and placed in a steel shipping container which was also in the dry box so that the powder ultimately was packaged in two hermetically sealed containers, both containing high purity argon as the cover gas.

Powder recovery efficiencies may be expressed in two ways - first, as a ratio of material charged to powder recovered, and second, as a ratio of material evaporated to powder recovered. The overall ratio of material charged to material recovered is a measure of the overall production efficiency of the system. The average efficiency of beryllium melt stock charged as compared with the powder collected was approximately 18%. The evaporation-collection efficiencies ranged from a low of 27% to a high of 61%.

The higher value indicates that of all the material evaporated, more was collected from the drum. Lower efficiencies indicate that less powder reached the drum and deposited instead on other parts of the tank and equipment which rendered recovery of the product inefficient. The exact cause for these variations in production was not determined and should be studied further.

Seven series of evaporation runs were conducted to produce approximately 400 grams of powder which was shipped to Nuclear Metals. Early in the program, it was determined that there was a slight amount of heat generated during the packaging operation which indicated either inleakage of moisture or oxygen from the atmosphere or diffusion of moisture through the gloves. The entire system was checked by a mass spectrometer for leaks and none were detected. Butyl rubber gloves were installed in the dry box and a recirculating argon purifying system was installed. The argon purifying system consisted of a hot titanium wire getter preceeded by a liquid nitrogen cold trap to remove moisture. After the installation of the argon purifying system, and the use of butyl rubber gloves, there was no further indication of reaction of the powder with the atmosphere during packaging.

F. Evaluation of Powder

The powder was shipped to Nuclear Metals in the containers described earlier. There it was compacted in a press, hermetically sealed in a steel container, and hot pressed. Samples of the hot pressed compact were analyzed spectrographically and the results are indicated in Table 13. For comparison, the analysis of the feed stock used to produce the powder is shown in Table 14. According to a comparison of the analyses, the two major contaminants determined spectrographically are lead and chromium. It is suspected that the lead came from some soft solder in the system, but this could not be confirmed. The chromium probably came from the stainless steel components of the system. In this case, nickel and iron should also be present, but, since they are present in the feed material, an increase is more difficult to detect.

Carbon and oxygen analysis on the powder showed that some contamination from both of these materials had occurred, although the data are not currently available. It was felt that the oxygen was primarily due to atmospheric exposure in handling either the bulk powder or the samples. The powder was reported to be extremely pyrophoric, as indicated when samples were exposed to air in the dry box during packaging. Personnel from Nuclear Metals have also reported that several samples of powder were lost by inadvertent exposure to air followed by typical pyrophoric combustion during handling. The carbon probably came from the carbon crucible source used for evaporation. Several modifications to the powder production equipment and procedure were instituted in an effort to improve the powder quality. Included in equipment modifications were:

TABLE 13

SPECTROGRAPHIC ANALYSIS OF HOT-PRESSED ULTRA-FINE GRAINED BERYLLIUM

Element	Estimated Content (ppm)	
	Light Area	Dark Area
Aluminum	>1000	>1000
Antimony	<10	<10
Calcium	≈100	≈100
Chromium	≈1000	≈1000
Cobalt	≈10	≈10
Copper	10-100	10-100
Iron	>1000	>1000
Lead	>1000	>1000
Magnesium	100-1000	100-1000
Manganese	100-1000	100-1000
Molybdenum	Present	Present
Nickel	100-1000	100-1000
Silicon	100-1000	100-1000
Silver	<10	<10
Sodium	500-1000	500-1000
Tin	≈10	≈10
Titanium	≈100	≈500
Vanadium	<10	<10
Zinc	≈100	≈100

TABLE 14

SPECTROGRAPHIC ANALYSIS OF QMV BERYLLIUM PEBBLE

Element	Estimated Content (%)
Beryllium Assay	99.0 (min.)
Beryllium Oxide	0.5 (max.)
Aluminum	0.14 (max.)
Boron	0.00020 (max.)
Cadmium	0.0002 (max.)
Calcium	0.02 (max.)
Carbon	0.14 (max.)
Chromium	0.03 (max.)
Cobalt	0.0005 (max.)
Copper	0.015 (max.)
Iron	0.15 (max.)
Lead	0.002 (max.)
Lithium	0.0003 (max.)
Magnesium	0.08 (max.)
Manganese	0.015 (max.)
Molybdenum	0.002 (max.)
Nickel	0.04 (max.)
Nitrogen	0.03 (max.)
Silicon	0.10 (max.)
Silver	0.0010 (max.)
Zinc	0.02 (max.)

(1) Installation of a liquid nitrogen trap between the powder production tank and oil diffusion tank to minimize the possibility of back-streaming of the oil from the diffusion pump and to trap water vapor in the system.

(2) Installation of a shield to prevent spatter of larger beryllium particles from the crucible assembly from entering the powder receiver during the initial part of the melt and early evaporation.

(3) Use of heavy polyethylene sheet inside the covers of the shipping jars in place of the thin Mylar sheet to provide a better and cleaner shield.

Changes in operation included:

(1) Use of beryllium oxide crucibles to eliminate carbon as a possible source of contamination and to prolong the evaporation cycle by eliminating the possibility of carbide formation.

(2) The discarding of the initial quantity of powder produced in each run. This would eliminate most of the larger particles produced in the initial start-up as the material melted in and spattered from the crucible. Also, the initial powder produced would act as a getter to remove any oxygen present in the atmosphere of the tank.

(3) The packaging of small samples of powder at the same time the larger samples were packaged to permit evaluation of each lot of powder as it is produced without extra handling which could possibly contaminate the sample further.

However, before any of these modifications and changes could be evaluated, the program was terminated by the sponsoring organization.

G. Particle Size Determination

No particle size or surface area determinations were conducted on the initial lot of powder. Electron micrograph examinations of powder produced after the initial lot were contemplated, but, because of the termination of the program, these determinations were never conducted.

For several years, National Research Corporation has been engaged in the production of ultra-fine metallic powders of aluminum, iron, nickel, and many others. The current program to produce beryllium powder was an extension of the work previously conducted. Basic techniques for producing beryllium powder are identical with those for producing other ultra-fine powders although, because of the hazardous nature of beryllium powder, special precautions were required to minimize the health hazard.

Ultra-fine aluminum and nickel powders have been studied extensively by electron microscopy and by surface area determination techniques. Particle sizes of aluminum and nickel powders are in the 200-600 Angstrom range with all particles less than 1000 Angstroms. The average particle diameter is about 300 Angstroms. Because the particles are less than the wavelength of visible

light (4000-7000 Angstroms), the powder is jet black - another indication of its very fine size. Surface area determinations by a modified BET procedure have indicated that both ultra-fine aluminum and nickel powders have surface areas of 20-30 square meters per gram. From these data, it is readily seen that individual particle size is well up in the sub-micron range.

Another property peculiar of ultra-fine metal powder is the extreme pyrophoricity when exposed to air. Aluminum in particular in the 200-600 Angstrom range is active and will readily ignite on exposure to air. The beryllium powder was also highly pyrophoric, as observed by those who produced it at National Research Corporation and by those who were engaged in compacting it at Nuclear Metals. When small quantities of beryllium powder were inadvertently exposed to air, they immediately flashed and burned. This is further indication that the beryllium powder is comparable to aluminum ultra-fine powder and the particle size is of the same order of magnitude.

Because the beryllium powder was produced under conditions essentially the same as ultra-fine nickel and aluminum powders, extrapolation of the properties, size, or surface area of the beryllium powders indicates beyond a reasonable doubt that the particle size range of the initial ultra-fine beryllium powder is essentially the same as the other metals produced.

H. Conclusions and Recommendations

The program has successfully demonstrated that ultra-fine beryllium powder can be produced by the method developed by National Research Corporation. One lot of approximately 400 grams of ultra-fine powder was produced and evaluated by Nuclear Metals, Inc. As a result of this evaluation, modifications were made to the powder production equipment to produce a still higher purity beryllium powder. It is unfortunate that more analytical data could not have been obtained from the initial quantities of powder evaluated. Electron micrographs were not taken; neither were surface area determinations conducted.

Modifications made to the powder producing equipment should reduce the oxygen, carbon, and the metallic contaminations in subsequent runs. We would recommend additional effort to evaluate the improvements anticipated from these changes. A higher purity feed stock should be utilized in order to arrive at a higher purity product. Additional high purity beryllium powder should be evaluated by production of compacts and hot pressing to determine whether or not the high purity powder will yield ductile beryllium. These compacts should be further examined by X-ray diffraction technology and by electron microscopy to determine the crystal structure and grain size. Before any beryllium powder is produced or packaged, a review of the evaluating procedures should be made so that sampling and analysis can be performed most efficiently. This will insure that sufficient samples, properly handled, in the most usable form are available and the sample and lot identity can be maintained throughout the program. It should be recognized that the overall program cost and operating efficiency will be enhanced if the work is undertaken in the near future rather than delayed for an extended period of time.

VI. FABRICATION AND EVALUATION OF ULTRA-FINE-GRAINED BERYLLIUM POWDERS

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A. Abstract

Procedures have been devised for the handling of ultra-fine beryllium powders under inert atmospheres. High-pressure cold-compaction, heliarc-welding of mild steel cans, and some chemical analysis procedures were carried out entirely under inert atmosphere. About one pound of ultra-fine powder was cold-compacted and hot-pressed, and the resulting cylinder was evaluated by mechanical, metallographic, chemical, and spectrographic methods. The hot-pressed material had exceptional hardness, but was also extremely brittle. A substantial impurity content was found, and a large number of relatively coarse impurity particles were observed metallographically, which might account to a large extent for the embrittlement of the hot-pressed material. Microhardness readings verified that the high hardness values were inherent to the fine powder material itself, and that the coarse impurity particles did not contribute significantly to this hardness. The compact also exhibited good high-temperature stability with respect to recrystallization and grain growth. It is felt that impurity levels can be substantially reduced by improved handling procedures, and recommendations are made for modifications of the present technique.

B. Introduction

It has been clearly demonstrated (Ref. 22) that the mechanical properties of beryllium are extremely sensitive to grain size. Both strength and ductility increase with decreasing grain size. It has also been shown (Ref. 23) that the third-dimensional ductility of beryllium under biaxial strains will increase with decreasing degree of preferred orientation of the material. It has been further demonstrated (Ref. 24) that increasing beryllium oxide content in the range of 2-10 w/o can reduce the degree of preferred orientation for a given fabrication procedure, although there is a corresponding loss in ductility. It seems reasonable, on the basis of an extrapolation of these facts, that a decrease in grain size to the one-micron range could result not only in the expected increases in strength values, but also in improved uniaxial and biaxial ductility.

Powder metallurgy is, at present, the only technique available for obtaining consistently fine grain sizes in beryllium products. By preparing and fabricating ultra-fine powders under inert atmosphere, not only would a fine grain size result, but a low oxygen-content-to-particle-surface-area ratio might be achieved which would improve interparticulate coherency, and might further improve ductility. After minimum oxygen levels had been established, controlled increases in oxygen content could be made, and the variations of properties with oxygen content and distribution could be determined.

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Because of the extremely fine size and low oxygen content of the powders expected to be produced in this study, the pyrophoric and toxic properties of these powders were a prime consideration in the development of handling procedures. The objective of the present program was twofold: first, to design and build facilities and develop procedures for the handling and fabrication of ultra-fine beryllium powders with maximum safety and minimum contamination; and, second, to evaluate the properties of these powders in both the as-received and fabricated states.

C. Experimental Procedures

1. Design and Construction of Pressing Facility

a. Original Facilities

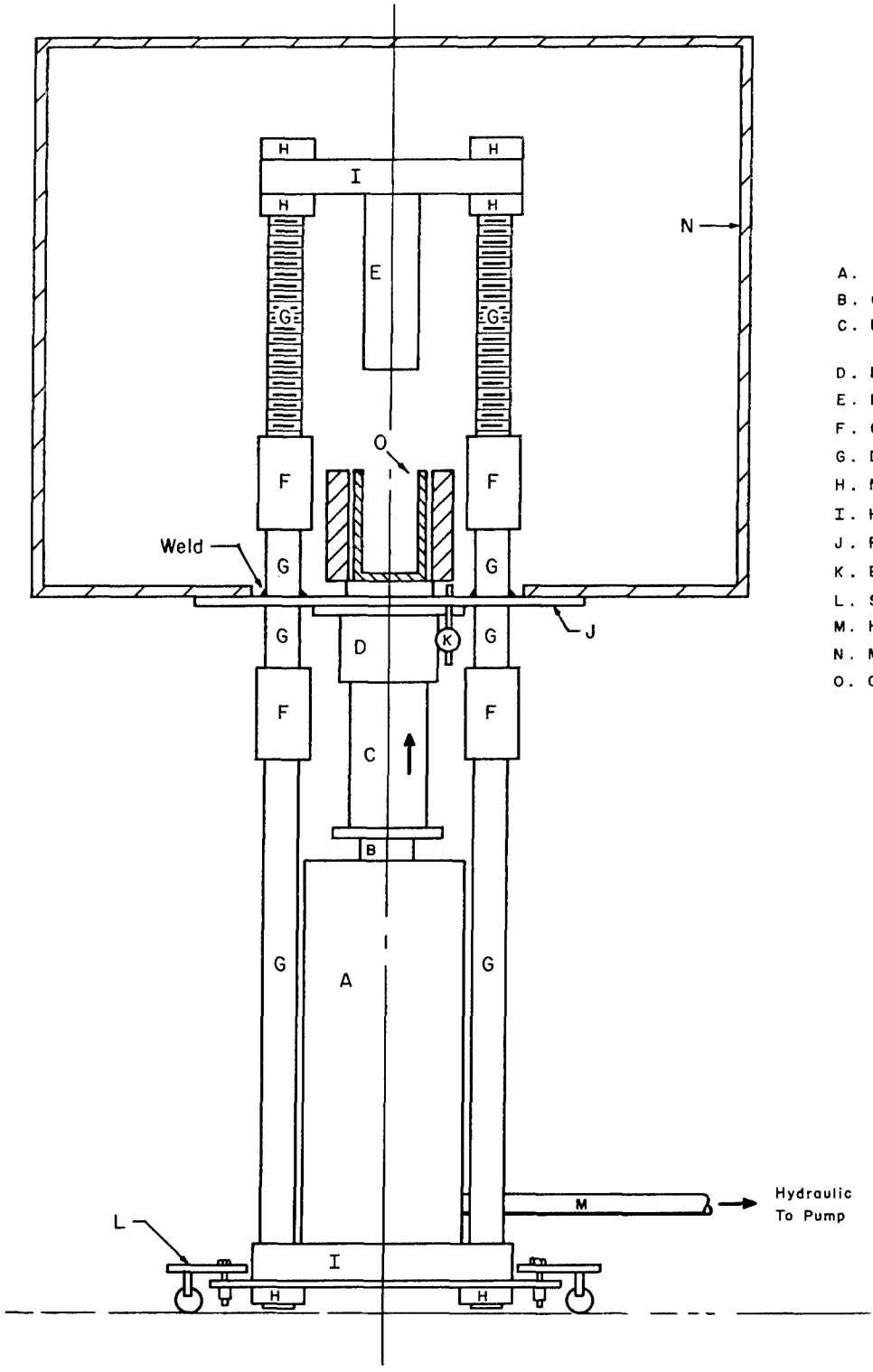
It was decided to build the inert atmosphere pressing apparatus into a glove box which consists of two separate units: a main chamber approximately 3 feet by 2 feet by 2 feet containing several viewing ports and glove facilities for a single operator; and an air lock which can be evacuated and pressurized independent of the main chamber, and through which materials may be introduced into the box without contaminating the atmosphere in the main chamber. Both chambers were linked by separate valve systems to a Kinney C-46 pump which is capable of evacuating the box to less than one-micron pressure. Separate valve systems are also present for introducing inert atmospheres into either chamber. A gas purification train circulates the inert atmosphere in the main chamber through a drying medium, a cold trap, and over a hot zirconium wire "getter", thereby minimizing oxygen and water vapor in the atmosphere.

b. Welding Equipment

In order to carry out the packing and canning operations, it was necessary to make several additions to the dry box facilities. It was required, first, to introduce equipment for heliarc-welding within the dry box under inert atmosphere. One of the glass viewing ports was removed and replaced by a steel fixture which accommodated a Teflon plate through which the water-cooled weld electrode was inserted into, and electrically insulated from, the dry box. The ground lead was attached directly to the exterior of the box, and all welding was carried out under purified helium atmosphere.

c. Inert Atmosphere Pressing Apparatus

A pressing facility was designed which would permit cold-compaction of the powders without danger of contamination from hydraulic fluids and without applying excessive stresses to the dry box itself. The design shown in Figure 26 consists of a self-contained pressing assembly with draw rods passing through, and welded to, a removable base plate in the bottom of the dry box. The load is transmitted by means of a hardened steel cylinder operating through a sliding seal in the base plate. Power is supplied with a 150-ton Rogers' hydraulic cylinder, which is pressurized with a 10,000 psi Vanguard electric pump. Each draw rod consists of three coupled sections which permit rapid assembly and disassembly of the upper and lower sections of the press. The cylinder is supported on a caster-mounted spring-loaded base which minimizes loading on the base plate of



A. 150 Ton Hydraulic Cylinder
B. Cylinder Plunger
C. Hardened Steel Sliding Cylinder with Restraining Collar
D. Brass Bushing with Sliding "O" Ring Seals
E. Packing Ram
F. Connectors
G. Draw Rods
H. Nuts
I. Hardened Steel Platens
J. Removable Base Plate
K. Billet Evacuation Tube with Ball Valve
L. Spring Loaded Portable Table
M. Hydraulic Hose
N. Main Chamber, Dry Box
O. Can - Packing Die

Fig. 26 - Schematic of inert-atmosphere press. Drawing No. RA-2366.

the main chamber and also prevents excessive stresses on the flooring beneath the dry box which might be caused by elastic straining and takeup of system slack during pressing. The position of the top platen is completely adjustable by means of retaining nuts, and both top and bottom platens can be leveled by means of these nuts to eliminate bending moments during pressing. A tube for outgassing and evacuation of welded cans containing cold-compacted powder is inserted through the base plate and is operated by a 1/4-inch ball valve.

The problem of maintaining a satisfactory vacuum at the sliding seal in the base of the dry box is solved by three O-rings on the ID of a brass bushing through which the close-fitting hardened steel cylinder slides. The selection of a draw rod material was based on the requirement that the material be capable of withstanding the high loading stresses and at the same time be weldable to the mild steel base plate without embrittlement or loss of strength. After careful consideration of various types of steels, a weld compatibility study was made employing 4150 steel rod and 1/4-inch boiler plate. The study demonstrated that, after normalizing, this rod could be welded without embrittlement or loss of strength. Accordingly, 1-1/2 inch diameter 4150 steel rods, normalized to yields in excess of 100,000 psi, were obtained for use as draw rods.

To eliminate the tendency of the sliding steel cylinder to be drawn into the box during evacuation, a tight-fitting retaining collar, fixed onto the steel cylinder by three set screws, was utilized.

2. Powder Handling Procedures

a. Transferral to Nuclear Metals, Inc.

The powders, which were produced at National Research Corporation (NRC) and New England Materials Laboratory (NEM Lab), were packed in glass jars having a screw-type cover which was sealed with electrical tape. After sealing these jars under inert atmosphere, they were sealed in metal containers, also under inert atmosphere, thereby providing a double barrier against contamination. The NEM Lab material, which was received in relatively small amounts for chemical analysis only, was forwarded in small vials, while the glass jars in which the powder from NRC was received were approximately 3 inches in diameter by 3 inches deep. In all cases, the glass jars were taken from the metal containers in the dry box and the metal cans were then taken out of the dry box through the air lock. In no case was more than 50 grams of powder packed in any one jar, and at no time was more than 50 grams of uncompacted powder exposed. All loose powder in excess of 50 grams was kept in the air lock in sealed glass jars during operations on the powder. It was felt that this precaution would greatly minimize the danger of a severe pyrophoric reaction in the event of accidental exposure to the air.

b. Chemical Analysis

Oxygen analysis was performed by the chloride volatilization technique on small isostatically compacted pellets (approximately 1/8-inch diameter by 1/8-inch high) supplied by NEM Lab. A reaction vessel was especially constructed so that it could be placed in the dry box. The pellet to be analyzed

was placed in a platinum boat in the reaction vessel under inert atmosphere, and the ends of the system were sealed with three-way glass valves. The reaction vessel was then removed from the dry box and inserted into the train of the HCl generation system. The system was carefully flushed with argon at both ends of the reaction vessel so that opening the valves would not introduce additional contamination. Analysis was then carried out by the standard volatilization technique.

Analysis for impurities other than oxygen was done by prior stabilization of the powder. In this case, the additional step of pelletizing the powder prior to analysis was not necessary. (Pellets were employed for the oxygen analysis because fine loose powders would be swept away in the HCl gas stream.) Stabilization was carried out in the following manner. The covers of the glass jars were removed under inert atmosphere and then loosely replaced. The chamber was then evacuated. The loosely applied cover permitted an adequate evacuation path but did not permit the powder to escape into the chamber. After evacuation, air was slowly bled into the dry box in small increments of pressure. After each increment was introduced, the samples were watched to determine if any burning was occurring. This technique was successfully employed to stabilize powders, so that they could subsequently be exposed to the air. It was then possible to remove the samples to the chemical laboratory where they could be analyzed by standard techniques. Iron, chromium, and nickel were determined by colorimetric analysis and carbon by conductimetric techniques.

c. Pyrophoricity of the Powder

In no case was any powder from NEM Lab exposed to the atmosphere. Consequently, no conclusions can be drawn regarding the pyrophoricity of this powder. However, the extremely pyrophoric nature of the NRC powder was inadvertently demonstrated. An attempt was made to stabilize a small amount of powder from each of the five lots supplied for cold-compaction by NRC. After the jars were removed from the dry box, it was found that three of the five covers were tightly sealed on the jars, indicating that the air had been bled into the dry box too rapidly during stabilization. The two jars which were not sealed did not exhibit any pyrophoric reaction. It was decided to open the three sealed jars under a hood approved for beryllium powder ventilation, since the amounts involved were extremely small (less than 5 grams). Upon exposure to the air, the powders became white hot within a few seconds, shattering the glass containers. Even those particles which had been successfully stabilized, when subjected to severe impact or heat, showed some flashing or burning, thereby indicating that the stability of these powders was extremely marginal.

The appearance of the as-received NEM Lab powder was typically metallic, although extremely fine and fluffy as compared with typical QMV powder. The NRC powder, on the other hand, was jet black. It was similar in appearance and consistency to graphite powder.

3. Packing and Pressing Procedure

a. Canning Materials

Canning material was machined from Shelby seamless tubing and boiler plate. The cans were 2.590-inch OD by 2.385-inch ID by 5-1/2 inches high. Base

plates were heliarc-welded to the cans. Evacuation tubes were welded to matching covers which were to be welded in place after packing. A hardened steel packing die, 4.475-inch OD by 2.610-inch ID, and a hardened steel packing ram, 2.365-inch diameter, were obtained. Mild steel spacers were machined which could be inserted between the end of the sliding cylinder and the walls of the die to permit ejection of the can from the die, employing the hydraulic press.

In order to facilitate pouring of the powders from the glass jars into the cans, a funnel-shaped pouring spout was made which could be interchanged with the original screw-type cover on the glass jar.

b. Preliminary Investigation Employing QMV Powder

In order to improve handling techniques and to point out unforeseen areas of difficulty, a preliminary packing experiment was carried out with QMV powder. Two hundred grams of powder were packed under a load of 75 tons. Approximately 40 grams per packing operation were employed. After packing, the can was welded shut, evacuated, and sealed. Sealing off was accomplished by pressing the evacuation tube flat (while still pumping on the billet) under a load of about 10 tons and then burning off the flattened area with a weld torch. Several difficulties were encountered during the packing operation, and the means devised to overcome them are noted below.

It was observed that, as the ram entered the can, loose powder was forced up the wall of the can because of the pressure built up ahead of the ram. After trying several different methods to contain this ejection, a technique employing a rubber seal was successfully applied. An O-ring, considerably smaller in diameter than the can ID, was stretched over the packing ram. When the ram was placed in the can, the O-ring was automatically brought up tightly against the can wall, thus effectively sealing the space between the can and the ram. This technique was very successful in preventing powder ejection, yet permitted passage of air during insertion of the ram.

After welding the can cover in place, an attempt was made to evacuate the billet under inert atmosphere. Failure to maintain an adequate vacuum indicated that leakage was occurring in the weld. By careful application of Apiezon compound, it was possible to locate the precise position of the leak and, after removal of the compound, to reweld this area and obtain a leak-free billet.

It was observed during welding that beryllium entered the weld zone, probably causing the porosity and leakage observed. Cleaning the ID of the can of loose powder with a cloth or brush was not an adequate solution to this problem. A mild steel disc, having a tapered outside diameter varying from 2.370 inches at the bottom to 2.400 inches at the top (diameter ID of can equals 2.385 inches), was forced into the top of the can employing the packing ram with a load of a few tons. This effectively forced all powder particles down ahead of the disc and prevented them from rising again into the weld zone. A hole in the center of the tapered disc permitted subsequent evacuation of the billet.

It was discovered that mild steel evacuation tubes tended to crack during flattening after evacuation, thereby destroying the vacuum in the billet.

On the other hand, stainless steel evacuation tubes, which could be easily substituted for the mild steel tubing, were readily cold-flattened without difficulty and could subsequently be heated and cut with the welding electrode without loss of vacuum.

c. Packing of Ultra-Fine Beryllium Powders Prepared by Vacuum Deposition

Five lots of ultra-fine powder, each lot weighing approximately 80 grams, were received from NRC. The lots had NRC designations 1 to 5, representing the chronological order of preparation. Each lot was divided about equally into two glass jars. The ten jars were stored in the air lock under inert atmosphere, and each jar was introduced into the main chamber (in numerical order), opened, poured, packed, and the empty jar replaced in the air lock. A small amount of powder from each of the five lots was retained in the loose state for chemical analysis (see paragraph C.2.b. above). An attempt was made to employ the same packing procedures (with the modifications previously noted) that were used for the QMV powder. However, several additional difficulties arose during handling of the ultra-fine powder. Due the extremely fluffy consistency of the ultra-fine powder, the pouring funnel, which had proved satisfactory for QMV powder, could not be used successfully. Considerable agitation of the jar was required to obtain even minimum flow rates of the powder, and this agitation resulted in excessive spillage. Pouring directly into the can was not feasible; first, because of the large jar diameter, and, second, because of the limited space between the top of the can and the bottom of the suspended packing ram. It was found, however, that, by removing the packing ram (which was supported by a threaded mild steel stud, which was in turn threaded into the top platen) and employing a camel's hair brush, the powder could be easily transferred from jar to can without any significant agitation or spillage.

Although the O-ring arrangements discussed in the previous section was entirely successful in preventing ejection of the ultra-fine powders during insertion of the ram, there was a tendency for the ram to "freeze" in the can after packing. This was presumably due to the entrapment of fine particles in the annulus between the ram and the can. However, by ejecting the can from the die after each pressing operation, it was possible to remove the ram from the can easily.

During the initial filling of the can, an entire jar of powder (approximately 40 grams) was poured and packed in a single operation. This yielded what appeared to be an extremely hard and coherent compact approximately 1/2-inch deep. In all instances, a 75-ton load was applied. As the available packing space decreased, it was no longer possible to pour an entire jar of the extremely fluffy powder into the can, and an increasing number of pouring and pressing operations was required to pack a single jar of powder. This procedure was further complicated by the necessity for ejecting the can from the die after each operation, which made the packing procedure extremely tedious. However, it was found that, by lightly tamping the powder with the packing ram, the amount of powder which could be poured prior to each full-pressure pressing operation was greatly increased, thereby alleviating the problem somewhat.

Due to the difficulties in maintaining surfaces free of beryllium powder within the dry box, the scoring of the can OD by the hardened die became

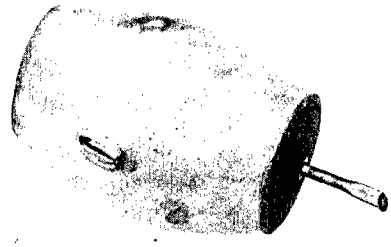
an increasing problem with each ejection from the packing die. This resulted in the need for increasingly high tonnages for each ejection procedure, and the need for careful handling of the rough-surfaced can to prevent cutting of the gloves. However, the most serious aspect of the scoring problem became apparent after welding had been completed. The use of the tapered disc had permitted a satisfactory weld to be applied, but subsequent attempts at outgassing indicated that a small leak was present. Apiezon sealing compound was applied in an attempt to locate the leak. However, after locating the leak, it was not possible to remove the Apiezon compound completely due to the scored and grooved outer surface of the can. Attempts at rewelding were impossible, due to interference of the sealing compound, and eventually resulted in a burn-through of the can wall. Since removal of the steel without exposure to the air was impractical, it was necessary to recan the entire billet. A mild steel can, 3.95-inch OD by 3-3/4-inch ID by 5-7/8-inches high, was machined and introduced into the dry box. The cold-compacted billet and the original can were placed in the new can and a cover welded on without incident. Evacuation of the billet under inert atmosphere to less than one micron verified that the weld was leak-tight, and the evacuation tube was flattened and cut with the welding electrode to form a vacuum-tight seal.

The recanned billet was removed from the dry box and transferred to a furnace at 1800°F preparatory to hot-pressing. A routine inspection of the billet after about 30 minutes in the furnace revealed that considerable swelling of the can had occurred. The can was immediately removed from the furnace and cooled under graphite. After cooling, the can was removed from the graphite, and a fracture in the side wall of the can was observed. It is not known at what stage in the heating and cooling this fracture occurred. A photograph of the can showing the swelling and cracking is presented in Figure 27. Calculation has shown that less than a monatomic layer of helium adsorbed on the powder when evolved at 1800°F could cause such fracture. Although the cold-compact was exposed to the air, no pyrophoric reaction was observed, indicating that the compact was sufficiently dense and coherent after fracture of the can to prevent oxidation below the compact surface. The outer can was cut away, revealing that no swelling had occurred of the inner can. Therefore, a new outer can was machined, and the original billet and can once again inserted and sealed by welding. This operation was not carried out in the dry box since additional exposure of the compact could not further affect it. Since the swelling of the original billet was undoubtedly due to a high temperature outgassing reaction, the new can was heated under vacuum at 1000°F for 24 hours. It was then sealed and heated to 1800°F without incident, followed by hot-pressing in a 1000-ton extrusion press. The mild steel cladding was pickled from the hot-pressing with dilute nitric acid.

D. Evaluation of Powder and Hot-Pressing

1. Physical Appearance of Hot-Pressing

A visual examination of the hot-pressed cylinder and of various sections through this cylinder revealed that the length of the cylinder was divided into alternately light and dark layers or discs. The sample was comprised of roughly ten of these layers, with the coloring of the light layer roughly comparable to that obtained in hot-pressed QMV powder, and the dark layer having considerably



RF-8878

Fig. 27 - Can containing cold-compacted ultrafine powders, evacuated at room temperature, sealed, and heated to 1800°F, showing swelling and rupture which occurred on heating.

less metallic luster. Although the layered structure was visible even in the as-pickled sample, a light etch in sulfuric acid greatly increased the contrast between the light and dark areas. Random cracking was apparent throughout the sample, but it appeared to be somewhat more prevalent in the darker areas.

2. Metallographic Studies

Several metallographic samples were taken from the hot-pressing, mounted in bakelite, and prepared for microscopic examination. It was found that the normal metallographic procedure of fine-polishing with a mixture of oxalic acid and alumina resulted in severe corrosion of the sample surface. A dispersion of alumina in distilled water was found to be a satisfactory polishing agent. The interface between the light and dark areas was clearly visible under bright light, as was the difference in coloration between these two areas. This is clearly shown in Figure 28. Both areas are basically composed of a "matrix" of generally unresolved beryllium particles, but the darker area appears to be characterized by a more porous structure. It is believed that this porosity is introduced during the sample preparation, and is not inherent in the structure.

Some relatively coarse microstructural features are observed in the fine powder matrix as shown in Figure 29. Some large spherical or oval particles are noted (with somewhat greater frequency in the dark area than in the light). These particles exhibit birefringency under polarized light and are believed to be large beryllium particles. The roughly spherical shape of these particles leads to the conclusion that they are formed during the original vapor-deposition process, rather than by any subsequent nucleation and/or growth process. Bright specks were frequently noted during the original pouring of the otherwise coal-black powder. It is believed that these specks are the large beryllium particles observed here which were of sufficient diameter to reflect light and exhibit a metallic luster. Still another metallographic feature observed was the presence of large angular particles, such as may be seen in Figure 29. These particles do not exhibit birefringency and appear to be extremely hard, as evidenced by the flow patterns of the material around them. Still another metallographic feature is the large number of fairly coherent "stringers" of material as seen at the bottom of Figure 29. These may have been large spherical beryllium particles which, since they would be extremely soft relative to the fine powder matrix, underwent considerable plastic flow due to their particular orientation or localized conditions in the pressing.

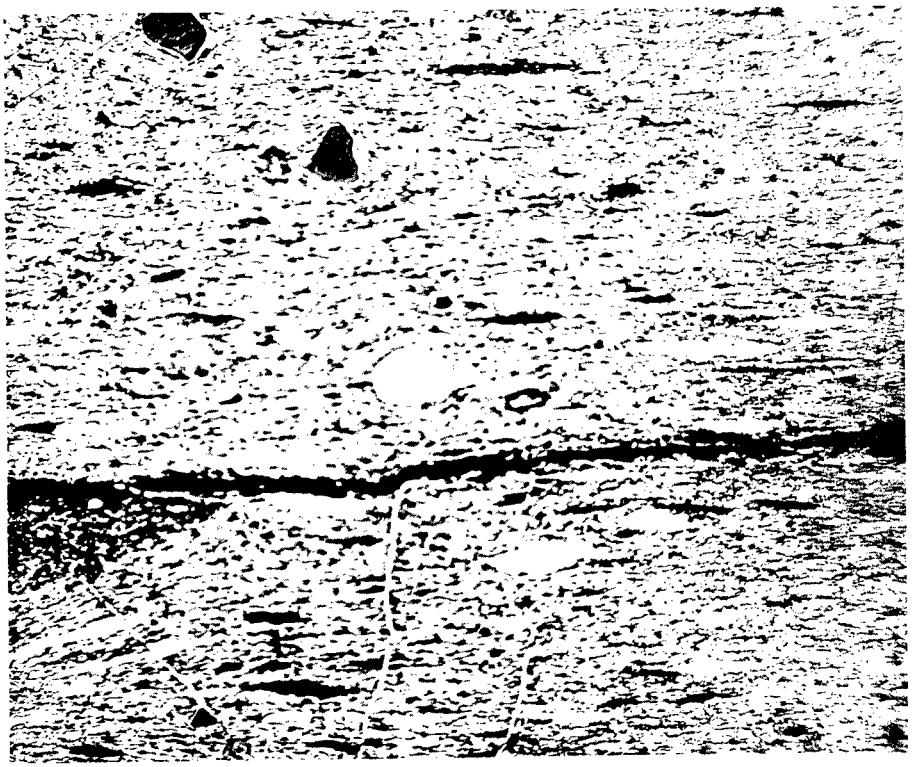
Since optical microscopy could not adequately resolve the fine powder structure, an attempt was made to induce grain growth by heat treating a sample at 1000°C for 24 hours. The treatment was carried out in sealed quartz tubing under a partial atmosphere of argon to prevent collapse of the tubing. Subsequent metallographic examination of these samples revealed that there had been no change in structure resulting from the heat treatment.

3. Hardness Studies

Both microhardness and macrohardness studies were made on both the dark and light areas of the hot-pressed ultra-fine powder.

50X Bt. Lt. B 495-2a

Fig.28 - Interface between light and dark areas of hot-pressed ultra-fine powders.



50X Bt. Lt. B 495-1a

Fig. 29 - Typical microstructural features of hot-pressed ultra-fine powders. Note white spherical particle (presumably beryllium), hard angular particles (presumably Be_2C), and unidentified white "stringers".

Microhardness readings were obtained with a Knoop indenter and, in most cases, a 500-gram load. Readings were taken in the fine-grained areas of both light and dark layers, and also in the individual coarse particles which were discussed above. The fine-grained area of the light zone had a hardness of 622 KHN, whereas the corresponding area of the dark zone had a hardness of 1009 KHN. A large angular inclusion, presumed to be Be_2C, had a hardness of 2115 KHN. The large spherical particles proved to be too soft for the 500-gram load, and a 25-gram load had to be substituted. The average hardness for two spherical particles was found to be 202 KHN.

Macrohardness readings were obtained with a Vickers hardness machine having a 30-kg load. The light area had an average hardness of 754 DPHN (high 778, low 720, average of eight readings). For the dark area, the average of seven readings was 857 DPHN with a high of 913 and a low of 787. These hardnesses are all much greater than any previously reported for beryllium. An examination of the hardness indentations in the dark area revealed that considerable cracking had occurred at the corners of the indentations, whereas no cracking occurred around indentations in the light area. In most cases, the cracks in the dark layers appear to propagate randomly a short distance into the surrounding matrix. However, in one case, a large spherical particle lay immediately adjacent to the corner of the hardness impression, and cracking in this particle appeared to be along distinct cleavage planes and propagated to the particle boundaries.

4. Chemical and Spectrographic Analyses

Determination of impurity content by both chemical and spectrographic techniques was carried out not only on the hot-pressed sample, but also on the as-received powder. The specific techniques employed in obtaining samples for chemical analysis from the as-received powder are outlined in the section on handling procedures. On the fully compacted billet, of course, no special handling procedures were required. All results of chemical analyses are presented in Table 15, and spectrographic results are presented in Table 16. Oxygen content was originally determined by a gravimetric technique involving chloride volatilization of the beryllium. However, because of the high level of other impurities, a photometric analysis for BeO was also carried out, which indicated that only about 75 percent of the residue measured in gravimetric analysis was actually BeO.

The results of chemical analysis on powder submitted by NEM Lab may be found in Section IV of this report.

It is apparent that all impurity levels are substantially higher than those obtained in normal QMV powder. While oxygen and carbon are the principal impurity constituents, iron, silicon, aluminum, and, surprisingly, lead are also exceptionally higher.

5. X-Ray Analysis

A section of the hot-pressed billet was mounted in bakelite, metallographically polished, and irradiated in a Norelco X-ray diffractometer under CuK_α radiation. In addition to the expected beryllium and BeO peaks, several strong unidentified impurity peaks were observed during a 2θ scan from 20 to 100 degrees. In an attempt to identify the elements or compounds responsible for these peaks, X-ray diffraction films were obtained for Debye-Scherrer powder

TABLE 15

CHEMICAL ANALYSES OF ULTRA-FINE POWDERS PREPARED
BY VAPOR DEPOSITION AT NATIONAL RESEARCH CORPORATION

Sample	Impurity Content				
	Fe (%)	C (%)	N (ppm)	B (ppm)	BeO (%)
1	0.205	2.50	--	--	--
2	1.31	3.22	--	--	--
3	0.175	--	--	--	--
4	--	5.10	1127	47	21.2*
5	--	4.10	427	86	19.4*
6	--	--	--	--	14.9**

1) As-received powder, stabilized in air, NRC Lot No. 1.

2) As-received powder, stabilized in air, NRC Lot No. 2.

3) As-received powder, stabilized in air, NRC Lot No. 3.

4) Hot-pressed powder, sample taken from light area.

5) Hot-pressed powder, sample taken from dark area.

6) Hot-pressed powder, sample not identified with respect to light and dark areas.

* Gravimetric - reflects all unvolatilized impurities.

** Photometric - reflects true BeO content.

TABLE 16

SPECTROGRAPHIC ANALYSES OF ULTRA-FINE POWDERS PREPARED BY VAPOR DEPOSITION

Sample	Impurity Content (ppm)									
	Fe	Sb	Ni	Cr	Mg	Mn	Si	Al	V	Co
A	>1000	<10	100-1000	≈1000	100-1000	100-1000	100-1000	>1000	<10	≈10
B	>1000	<10	100-1000	≈1000	100-1000	100-1000	100-1000	>1000	<10	≈10
C	>1000	<10	≈1000	≈1000	100-1000	100-1000	>1000	>1000	≈10	≈10
D	>1000*	<10*	>1000	>1000	100-1000	100-1000*	>1000	>1000	≈10*	10-100
	Cu	Ag	Pb	Ti	Sn	Zn	Na	Mo	Ca	B
A	10-100	<10	>1000	≈100	≈10	≈100	500-1000	Present	≈100	—
B	10-100	<10	>1000	≈500	≈10	≈100	500-1000	Present	≈100	—
C	100-500	<10	>1000	≈100	10-100	100-1000	≈1000	<10	500-1000	≈100*
D	100-500	<10	≈1000	100-500	≈100	10-100	≈1000	≈10	500-1000	≈100

A - Sample taken from light area of hot pressing.

B - Sample taken from dark area of hot pressing.

C - As-received powder, stabilized in air, NRC Lot No. 1.

D - As-received powder, stabilized in air, NRC Lot No. 2.

* Greater of the two (C and D)

samples prepared from the hot-pressing, the as-received powder, and from a residue obtained during dissolution of the hot-pressed powder to determine boron content. Although a large number of impurity traces were observed by this technique, the only impurities which could be definitely indexed were BeO and Be_2C.

6. Tensile Sample Preparation

An attempt was made to determine the tensile properties of the hot-pressed block. Sample blanks were cut at right angles to the pressing axis from crack-free areas of the hot-pressing. Of the eight blanks available, all but one were entirely within the light layers of the hot-pressing. The remaining sample lay across a dark and light area, with the interface of the layer intersecting the gauge length region of the blank. It was intended to machine small cylindrical samples from these blanks and, due to their demonstrated high hardness, it was felt that grinding would be less likely to initiate brittle failure than a turning operation. However, even when removing very small amounts of material per pass by grinding, the samples fractured before the final dimensions could be achieved. In view of this extreme brittle behavior and the lack of feasibility of obtaining tensile samples by normal machining procedures, it was decided to discontinue the tensile studies.

E. Discussion and Recommendations

1. Quality of the As-Received Powder

a. Powder Ball-Milled at NEM Lab

A complete description of the preparation and chemical evaluation of this material is presented in Section IV of this report. No attempt was made to cold-compact or fabricate this material primarily because of the extremely high iron and chromium contents observed in samples submitted by NEM Lab. However, the coherency of the isostatically compacted pellets submitted for oxygen analysis indicated that cold-compaction of this powder is feasible. It was demonstrated that routine handling procedures may be readily carried out under inert atmosphere conditions, and it is anticipated that fabrication of this powder would present no difficulties beyond those encountered with the NRC powder. The primary consideration at this time, therefore, seems to be to reduce the impurity content of the material sufficiently to justify the evaluation of subsequent consolidation procedures. Probably the only significant sources of contamination are the mill lining, the grinding balls, and the grinding fluid. It would, therefore, seem that a judicious choice of materials and/or media could readily eliminate the bulk of this problem. Recent experiments have been conducted using a beryllium lined mill. The powder produced from this has not as yet been evaluated.

b. Powder Prepared by Vapor Deposition at NRC

The black graphite-like appearance of the NRC powder attests to its extremely small particle size. The occasional bright specks observed in the powder are almost undoubtedly coarse beryllium particles formed during the vapor-deposition process. This conclusion is substantiated by metallographic observations of spherical particles which exhibit extreme softness, birefringency, and pronounced cleavage patterns. Although it is possible that these particles might be removed by a screening operation, they represent an extremely small volume percent of the total material and may have a negligible effect on

the properties of the much harder matrix. As was observed for NEM Lab powder, the oxide contents are appreciably higher than those observed in QMV powder (see Table 15). However, there is no question that the oxidation of this material is greatly inhibited by the inert atmosphere handling procedures and that the oxide layer on each particle is considerably thinner and/or less continuous than that existing on QMV powder. For instance, if the powder prepared by vapor deposition were fully oxidized (assuming an oxide layer thickness equal to that on QMV powder), the oxide content would be in excess of 90 percent.

The other impurities listed in Table 15 also exhibit relatively high levels of contamination. The as-received powder contained an exceptionally large amount of carbon. Backstreaming of oil from the diffusion pump during vaporization might introduce carbon contamination. Although a boron nitride wash was employed on the graphite crucible used in the original vaporization process, it is possible that there was sufficient breakdown of this wash to permit substantial carbon contamination from the crucible. The fact that both boron and nitrogen contents are higher than anticipated in the compacted material is further indication that the boron nitride wash might not provide adequate protection. In particular, it is difficult to envision any other source of boron contamination.

The iron content, while not showing gross contamination, is nevertheless about double that normally encountered in QMV powder. The single high value of 1.3 percent probably does not reflect the true iron content, but rather the presence of an isolated iron particle in the analysis sample. A possible source of iron contamination might be the brushing of the powders with a steel brush from the rotating steel drum. The source of other relatively high impurities, such as aluminum and lead, is less apparent and may be traceable to later stages in the handling of the powder.

It would seem that the primary problem to be overcome in preparation of the vapor-deposited powder is carbon contamination. Although it is well known that the addition of small amounts of iron exert an embrittling effect on beryllium, the present iron content might be considered to be marginally acceptable and could probably be reduced to still more acceptable levels without undue difficulty.

2. Quality of the Hot-Pressed Block

The most prominent features of the hot-pressed ultra-fine powder billet are its extreme hardness and severe embrittlement. Microhardness readings demonstrated that the high hardness was an inherent property of the aggregate of fine particles (although undoubtedly influenced to some extent by the oxide layer on these particles) and not associated with the coarser microstructural features. On the other hand, it is possible that the brittleness problem might be somewhat alleviated by the elimination of these coarse particles.

Metallographic studies showed that there was no overall polarization effect of the fine particles, indicating the essential randomness of the structure, as would be expected for hot-pressed material. This observation, plus the apparently random direction of crack propagation, verifies that the observed

fractures are not texture induced. A possible source of brittleness might be lack of interparticulate coherency. However, even hot-pressed QMV powder exhibits a moderate amount of ductility, despite a larger oxide-to-particle-surface-area ratio, which would tend to inhibit cohesion. Moreover, the cold-compacted surfaces of the ultra-fine powders appear to be more coherent and resistant to chipping or scratching than surfaces obtained under comparable loads with QMV powder. The estimated cold-compaction density of 70 percent for the NRC ultra-fine powder is comparable to cold-compaction densities obtained for QMV powder, even at considerably higher stress levels. Although the particle size, per se, may result in embrittlement of the hot-pressed compact, an extrapolation of data for larger grain and/or particle sizes of beryllium indicates that the reverse should be true (i.e., that decreasing particle size results in increased ductility). The severe embrittlement of beryllium by relatively small amounts of impurities is well documented. It, therefore, seems logical to conclude that the primary cause of the observed embrittlement of the hot-pressed block is the excessively high impurity content. Carbon, in the form of coarse Be_2C particles, or in a fine network, is particularly suspect. It is probable that, if impurity contents could be maintained at more reasonable levels, a product of acceptable ductility and exceptional strength and hardness would result.

It is felt that the loss of close tolerances and good fit occasioned by recanning the original billet are primarily responsible for the cracking observed in the hot-pressed powder compact. Although tensile samples were taken from areas which were apparently crack-free, it is possible that widespread microcracking also occurred during hot-pressing, and this may have contributed substantially to the observed brittleness.

The stability of the hot-pressing with respect to grain growth and recrystallization has been demonstrated. However, such stability is typical of hot-pressed samples where oxide boundaries are not broken down during the pressing operation. A process requiring more plastic flow of the material, such as extrusion, would be required to verify the high-temperature stability of the fine-grained material.

The problem of the source of the light and dark layers throughout the hot-pressed cylinder is not easily resolved. The higher hardness of the darker areas would lead to the suspicion that these areas were denser, more coherent, finer structured, or contained a greater amount of a hard dispersed phase. These assumptions would be further strengthened by the increased tendency to propagate cracks in the dark areas. However, metallographic studies indicate that the darker area is not observably finer than the light, that it is more porous, and that only the soft spheroidal particles are more frequently observed than in the light phase. Moreover, the darker appearance of this area implies that the structure is less coherent and that the light reflection properties of this area are more typical of the reflectivity of individual particles, rather than of a coherent metallic structure. The chemical analyses of the light areas indicate a slightly higher impurity content than the dark areas, with the exception of boron, and consequently an expected higher hardness in the light area. It is probable that the source of this anomaly is the packing procedure, and that the problem could be alleviated by improved handling techniques.

Spectrographic analyses of as-received powders and sections of the hot-pressed sample indicated that there was little significant increase in overall impurity level during the packing and hot-pressing operations. However, the carbon content, although extremely high in the as-received powder, is increased significantly after processing as indicated by chemical analyses, and this difference is presumably due to the exposure after swelling and fracture of the can. Although no values are available for the as-received oxide content of the NRC material, it is presumed that the inadvertent exposure also resulted in some increase in BeO content.

3. Handling and Fabrication Techniques

In view of the demonstrated ability of the NRC ultra-fine powders to be cold-compacted and hot-pressed, it is felt that the primary objective of the handling and fabricated procedures is to minimize the handling time while still maintaining maximum precautions to avoid contamination or safety hazards. For both the NEM Lab and NRC powders, the oxide content is probably a function of purity of the surrounding atmosphere, time and temperature of exposure during preparation, and time of exposure between preparation and fabrication. As the presence of reactive elements in the atmosphere is lowered, the importance of the last two factors also decreases. However, there are practical and economic limitations to atmospheric purity. The time and temperature (even during room-temperature attritioning, extremely high localized temperatures may be achieved where particles fracture) of exposure during preparation can probably not be altered substantially in the present techniques without compromising the resulting particle size. Because many of the unique difficulties in handling ultra-fine powders only became apparent after they had been encountered in the actual fabrication operation, it is felt that the handling time after preparation can be greatly reduced.

First, it is felt that, for developmental purposes, the amount of material handled in a single hot-pressing operation should be substantially reduced to, say, 50 grams. The reasons for this are several. The fact that the can must be ejected from the die after each loading operation makes it desirable to minimize the number of pressing operations required to obtain a fabricated billet. Fifty grams of powder can be pressed in a single operation. Since scoring of the can may occur during repeated ejection operations, a single pressing will also minimize the chance of iron contamination. It is also expected that the alternate layer problem would be removed by a single pressing operation. Although a 4- to 5-inch high can is still required for pouring space of the 50 grams of powder (which would result in a compact about 1/2-inch high), the remaining can space may be filled with a dummy material, such as mild steel. The lessened opportunity for can damage will also result in cleaner, more reliable welds. Not only does the use of a smaller amount of powder eliminate a "lag" period for uncompacted powders sitting in the dry box, but the smaller amount of powder may also be produced in a single lot, which can be transferred immediately to Nuclear Metals without waiting for subsequent vapor-deposition runs.

The improved weld reliability, which would result from smaller fabrication lots, would minimize the necessity for leak detection. It is, nevertheless, apparent that a more reliable technique is required for leak detection.

The dry box has been modified so that it may be filled with a high-purity argon atmosphere, and the welded can may be evacuated while small controlled amounts of helium are introduced into the box. A mass spectrometer leak detector may then be employed to detect the presence of helium entering the billet evacuation system.

The fact that high-temperature outgassing of the billet is required prior to sealing has been conclusively demonstrated. It is therefore recommended that, after a leak-tight weld has been obtained on the can cover, the compact be transferred to a high-temperature, high-vacuum outgassing facility. This transfer can be safely accomplished by means of a small ball valve on the evacuation tube. The billet may be slightly pressurized with inert atmosphere prior to removal from the box to minimize the chance of contamination further during transfer.

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