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ASD-TDR-62-1018

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SOLUBILITY AND DIFFUSION OF GASES IN BERYLLIUM

TECHNICAL DOCUMENTARY REPORT NO. ASD-TDR-62-1018

February 1963

Directorate of Materials and Processes
Aeronautical Systems Division
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

Project No. 7360, Task No. 736005

(Prepared under Contract No. AF 33(616)-7665 by Nuclear Metals, Inc., Concord, Massachusetts; J. P. Peisler, R. W. Anderson and E. J. Rappaport, Authors)

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FOREWORD

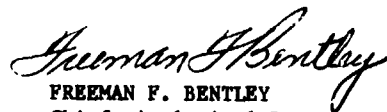
This report was prepared by Nuclear Metals, Inc., under USAF Contract No. AF 33(616)-/665. This contract was initiated under Project No. 7360, "The Chemistry and Physics of Materials", Task No. 736005, "Compositional, Atomic and Molecular Analysis". The work was administered under the direction of the Directorate of Materials and Processes, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio, with C. D. Houston acting as project engineer.

This report covers work conducted from November 1960 to October 1961.

ABSTRACT

Results of an experimental program to determine the solubility and diffusion rate of nitrogen, hydrogen, and oxygen in beryllium are reported. The solubility of nitrogen in beryllium at 1000°C is estimated to be about 60 ppm; this value appears to be temperature independent. The results of nitrogen diffusion experiments are considered tentative. The solubility of hydrogen in beryllium is believed to be very small. Measurement of the growth characteristics of hydrogen bubbles formed in beryllium by proton bombardment indicate a value for the diffusion coefficient of hydrogen in beryllium of 9×10^{-10} cm²/sec at 850°C. Due to limitations of chemical analysis, no new data concerning the beryllium-oxygen system was obtained.

This technical documentary report has been reviewed and is approved.



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I. INTRODUCTION

The technology of beryllium is under investigation on several fronts. The mechanical properties of the metal are known to be dependent on impurity content, and on the size and orientation of the grains in polycrystalline material. The gaseous impurities, O_2 , N_2 and H_2 , have been found to be extremely important in affecting the properties of many metals. However, data on the effect of these impurities on the mechanical properties of beryllium are lacking, and the solubilities and diffusion rates of these gases in beryllium have not been determined. The reasons for the lack of data in this regard are: (1) oxygen and nitrogen are very slightly soluble in solid beryllium and form compounds readily, and (2) hydrogen is only slightly soluble and the existence of a beryllium hydride in the solid phase is doubtful. These characteristics, coupled with the fact that, in the case of oxygen, the analytical techniques are not considered reliable, make the study of these gaseous impurities in beryllium exceedingly difficult. This work was performed to develop techniques for studying several basic features of the interactions of beryllium with these gases.

II. LITERATURE SURVEY

A literature survey prepared at the initiation of this program to aid in the planning of experiments was issued as a separate document (NMI-9805).

III. NITROGEN

A. Solubility of Nitrogen in Beryllium

1. Experiments

Beryllium samples with various nitrogen contents were prepared by melting Pechiney flake beryllium with a Be-Be₃N₂ master alloy. The beryllium-nitrogen master alloys were prepared by nitriding Pechiney flake beryllium in a BeO crucible supported within a quartz tube which was connected to a vacuum system. The system was evacuated and purified nitrogen admitted to a pressure of 20 mm Hg. The nitrogen was purified by passing it over hot zirconium chips and then through a liquid nitrogen cold trap. The quartz tube containing the sample was placed in a platinum-wound resistance furnace heated to 1000°C, and the sample was held at temperature for about five hours. Bulk nitrogen contents of about 3% were obtained by this method. Some sintering of the material resulted during nitriding, but the aggregate was readily reduced to powder by crushing. To obtain higher nitrogen concentrations it was necessary to first expose new surfaces by grinding the material and then to renitride.

Two methods of melting the beryllium-nitrogen alloys were investigated.

(a) Button Arc Melting. Pure beryllium mixed with various amounts of beryllium-nitrogen master alloy was cold compacted to 1/2-inch diameter buttons. The buttons were arc melted on a water-cooled copper hearth with a tungsten electrode. The quartz furnace container was evacuated and back filled with argon before melting. The button was melted five times; after each melt the button was turned over to aid in obtaining a homogeneous sample. Chemical analysis indicated that essentially all of the nitrogen was recovered, but the button was contaminated with tungsten,

apparently from the electrode. This method was not investigated further, because of the contamination problem.

(b) Induction Melting. Pure beryllium flake mixed with various amounts of beryllium-nitrogen master alloy was induction melted in a covered BeO thermal-analysis crucible. The temperature was measured with a platinum-10% rhodium thermocouple protected from beryllium vapor contamination by a thin beryllium oxide coating. The temperature was recorded on a Leeds and Northrup Speedomax type G strip recorder. Pressures of less than one micron Hg were maintained during melting. The beryllium-nitrogen alloy reacted very slowly with the pure beryllium. The amount of the nitrogen that was dissolved into the melt was controlled primarily by the time and temperature above the melting point, rather than by the amount of the nitride present. Attempts to melt nitrided particles without pure beryllium present at temperatures as high as 1600°C resulted in only partial melting. Apparently the nitride surface layer surrounding each particle effectively contained the molten beryllium core. Evidence that the core of the particles had melted was obtained by the thermal arrests in the cooling curves.

Beryllium-nitrogen specimens were analyzed for nitrogen content by the micro-Kjeldahl method. The surfaces of the half-gram samples used for analysis were cleaned by wire brushing and etched in dilute sulfuric acid prior to analysis. This was done to remove any surface nitride. Metallographic examination was performed on areas of the sample adjacent to the area from which samples were taken for chemical analysis.

Specimens containing relatively large amounts of nitrogen were used in a preliminary study to identify the Be_3N_2 phase in the beryllium matrix. (No other beryllium-nitrogen phase has been identified). Metallographic procedures used for the preparation of the specimens were as follows: (1) wet grind on successively finer silicon-carbide papers to 600 grit, (2) rough polish on a silk cloth wheel with "Linde A" in distilled water, (3) final polish on a "micro-cloth" wheel with "Linde B" in distilled water, and (4) lightly etch with one percent HF in water to remove disturbed surface layers. The results of this study indicated that the shape of the Be_3N_2 phase is dependent on the freezing rate. Rapid quenching results in an acicular or needlelike phase, whereas slow cooling produces globular particles. In both cases the phase is semitransparent, with a blue-grey cast in both the etched or unetched condition. The nitride precipitate is not active in polarized light, nor is it attacked rapidly by the etchant. However, a black surface layer forms on the Be_3N_2 if the specimen is exposed to ambient laboratory atmosphere for several days. The nitride phase is, therefore, readily identified in a beryllium matrix and can be detected in the presence of such impurities as carbides and aluminum and silicon compounds.

In conjunction with the induction melting of the beryllium-nitrogen specimen, the transformation temperatures of several compositions were measured. A resistance-heated furnace with the controlled heating and cooling rates of 4°C per minute was used. The specimens were heated in argon at reduced pressures in order to suppress evaporation of the beryllium.

2. Results

(a) Solubility Measurements. The specimens listed in Table I

were used to estimate the solubility limit of nitrogen in beryllium. Metallographic detection of the Be_3N_2 phase in beryllium was used as evidence that the nitrogen solubility was exceeded. An approximate value of the solubility limit, which lies between 48 and 73 ppm, was obtained by examination of the as-cast specimens. These specimens, containing nitrogen in the range of 48 to 600 ppm, were annealed in vacuum at 1000°C for times of 8 and 56 hours in an effort to obtain an equilibrium structure. Higher equilibrating temperatures were not feasible because of the high vapor pressure of beryllium. The solubility limit of the annealed specimens was again found to lie between 48 and 73 ppm. No depletion or spheroidization of the nitride phase was detected. Sections of the specimens equilibrated at 1000°C were subsequently heat treated for 196 hours at 500 and 800°C in an attempt to determine the effect of temperature on the solubility. Precipitation of the nitride phase from solid solution was not detected at either of these lower temperatures.

From these results, the following conclusions can be drawn: (1) as determined by chemical and metallographic analysis, the solubility of nitrogen in beryllium at 1000°C (and probably to the melting point, 1283°C) lies between 48 and 73 ppm, and (2) there is no detectable change in the solubility between 1000 and 500°C .

(b) Thermal Arrest Measurements. Thermal arrest data are presented in Table II. No data are available from runs 12A and 13A, since the alloy was not completely molten at a temperature of 1360°C . The slope change during heating is attributed to the slow dissolution of the nitride phase. These preliminary data indicate that nitrogen lowers the melting point and the alpha-to-beta transformation temperature of beryllium.

B. Diffusion of Nitrogen in Beryllium

1. Experiments

Attempts to measure the rate of diffusion of nitrogen in beryllium were made using a beryllium-beryllium nitride diffusion couple. A beryllium slab, 5 cm x 3.5 cm x 0.8 cm, was ground so that the large faces were flat and parallel. The slab was then supported on a BeO plate in a horizontal quartz tube attached to a vacuum system. The system was evacuated to less than $0.1\ \mu\text{-Hg}$ and purified nitrogen was admitted to a pressure of one atmosphere. The tube was then placed into a sliding horizontal furnace, and the temperature of the furnace increased to about 975°C . Samples were nitrized for one-half to one hour and then air cooled. A thin nitride layer resulted.

The sample was removed from the quartz tube and re-seated on a BeO plate contained within a tantalum cylinder. The cylinder was placed within a quartz tube which was evacuated, filled with purified argon to 150 mm Hg and sealed off. The tantalum served to prevent interaction between vaporized beryllium and quartz, which would lead to the formation of volatile silicon oxides. The assembly is shown in Fig. 1. The tube was heated to 1025°C and held at temperature for 17 days. After the diffusion anneal was completed, the sample was furnace cooled.

Three-mil deep cuts were then milled from each side of the slab and the chips collected separately. Extreme precautions were taken to thoroughly degrease all surfaces and tools coming in contact with the beryllium slab. These precautions were also used in handling the chips. Prior to milling, the edges of the slab were

ground to a depth of 10 mils to avoid nitride contamination of the chips by material from the edges. About 0.2 grams of chips were collected from each 3-mil cut. The chips were then analyzed for nitrogen by the micro-Kjeldahl technique.

2. Results

Initial experiments were carried out on slabs machined from vacuum-melted Pechiney flake. Microscopic examination of the slab after machining indicated that appreciable microporosity existed in the casting and that the pores extended to depths of 10 to 15 mils. Since these pores were exposed to the nitrogen atmosphere and developed a nitride film, they represent sources of considerable nitrogen contamination in the metal substrate. This contamination is sufficient to obscure any nitrogen gradient which might be present in the solid metal substrate. It was further found that, if the nitride layer which formed on the beryllium sample became too thick, it became nonadherent during the diffusion anneal and lifted away from the beryllium substrate. This had the effect of removing the source of nitrogen from the beryllium surface and thereby destroying the diffusion couple.

In order to eliminate porosity in the casting, a billet of melted Pechiney flake was extruded to a flat with a reduction in area of about 8 to 1. A successful experiment was performed on extruded material wherein a nitride layer formed on the beryllium and remained closely adherent during the diffusion anneal. The data are presented in Table III and plotted in Fig. 2. The concentration of nitrogen in the initial 3-mil cut of metal is not plotted in the Figure, since it includes nitrogen derived from the nitride layer.

The diffusion coefficient of nitrogen in beryllium can be readily calculated from these data and a knowledge of the solubility of nitrogen in beryllium (see the preceding section). Mathematically the experiment falls within the class of diffusion into a semi-infinite medium with a fixed concentration of nitrogen at the metal-nitride boundary.

The boundary conditions are expressed as:

for $t = 0$

$$\begin{aligned} c &= c_g & \text{for } x < 0 \\ c &= c_1 & \text{for } x = 0 \end{aligned} \quad (1)$$

and for $t > 0$

$$\begin{aligned} c &= c_g & \text{for } x < 0 \\ c_g &\geq c > c_1 & \text{for } x \geq 0 \end{aligned} \quad (2)$$

where c = concentration of nitrogen in beryllium at a distance x from the beryllium-beryllium nitride interface,

c_s = the saturation solubility of nitrogen in beryllium, and

c_i = the initial concentration of nitrogen in beryllium.

The solution to this equation⁽¹⁾ is given by:

$$\frac{c_s - c}{c_s - c_i} = \text{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \quad (3)$$

where D = diffusion coefficient of nitrogen in beryllium at the temperature of the experiment, and

t = time,

In this case, the saturation concentration is taken from the previous section as $c_s = 1.10 \times 10^{-4}$ g/cm³, and the initial nitrogen concentration in the metal is taken as $c_i = 0$.

The above equation is best solved for D by plotting

$$\text{erf}^{-1} \left(\frac{c_s - c}{c_s} \right) \text{ vs. } \frac{x}{2\sqrt{t}}$$

Such a plot is shown in Fig. 3.

The slope, m , of the best line drawn through the data points is related to the diffusion coefficient by

$$m = \frac{1}{\sqrt{D}} \quad (4)$$

The value calculated by this technique based on a single successful experiment is $D \sim 5 \times 10^{-10}$ cm²/sec. This value seems high when compared with the value obtained for hydrogen in beryllium (see Section IV) since it would be expected that hydrogen would diffuse in beryllium at a considerably faster rate than nitrogen.

The most likely sources of error in this experiment are:

- (1) Residual microporosity in the extruded rod contributing nitride to layers below the surface, and
- (2) Contamination from machining and handling.

It is apparent that additional experiments must be performed before the value for the diffusion coefficient is accepted.

IV. HYDROGEN

Previous investigators have found that the solubility of hydrogen in beryllium

is very small. Gulbransen and Andrew⁽²⁾ state that beryllium does not react with hydrogen at 300 to 900°C and 23 mm Hg. Cotterill et al.⁽³⁾ report that as-machined beryllium has an adsorbed hydrogen layer of $\sim 0.007 \text{ cm}^3/\text{cm}^2$ of surface. No additional hydrogen is picked up either in an atmosphere of 0.1 mm Hg pressure at temperatures of 20°C to 800°C, or when hydrogen is bubbled through a melt. Beryllium hydride has been reported to exist in an ether solution^(4,5), but decomposes at about 200°C; there is no convincing evidence for the existence of the hydride in the solid phase.

A. Experimental

In order to prepare specimens with various known hydrogen contents, it was necessary to generate the hydrogen within the beryllium lattice by means of proton bombardment. Proton irradiation was performed in the MIT cyclotron where a 7.5 Mev proton beam was available. Specimens 0.100 cm thick, 12.75 cm long and 1.27 cm wide were ground from an extruded flat of high-purity distilled metal.⁽⁶⁾ A typical analysis of the distilled metal is given in Table IV. The sample holder shown in Fig. 4 is a modification of the design used at MIT. The cooling water passing through the sample holder maintained sample temperature below 50°C during irradiation.⁽⁷⁾ Samples were exposed to a 10 microampere proton beam for three different time intervals: 0.17, 1.70 and 17.00 hours.

B. Results

The proton beam penetrated the beryllium to a depth of 0.040 cm and formed a layer of hydrogen-containing metal about 0.004 cm thick. Hydrogen concentrations of 0.00075, 0.0075 and 0.075 a/o, corresponding to exposures of 1.7, 17 and 170 microampere-hours, were achieved in the narrow hydrogen-containing band of the sample. (See Appendix for this calculation.)

No evidence of hydrogen agglomeration was found in the as-bombarded samples after mechanical polishing and etching. However, post-bombardment heat treatment led to the formation of agglomerates readily visible under optical magnification. At annealing temperatures below 700°C, it was also necessary to etch samples in order to observe the agglomerates. Ellis and Evans have recently reported⁽⁷⁾ that the heat treatment necessary to give agglomerates that could be observed by optical microscopy is dependent on the purity and history of the specimen. The etchant used consisted of a 10 percent solution of HF in glycerine, with etching times of one minute. Figures 5 through 10 show the 0.075 a/o sample (170 microampere-hours exposure) after annealing for one hour at various temperatures. One-half of the sample in Fig. 11 received an exposure of 1.7 microampere-hours; the other half received 17 microampere-hours.

At 350°C the agglomerates are readily visible and show a tendency to nucleate at grain boundaries and other areas of stress. At higher temperatures, the agglomerates coarsen and migrate to grain boundaries. Figure 10, taken in polarized light, clearly shows the agglomerates preponderantly residing at grain boundaries. This suggests a more rapid diffusion of hydrogen along the grain boundaries than through the lattice. At 900°C there is evidence of depletion of hydrogen due to dispersal from both the matrix and grain boundaries. After one hour at 1050°C, no hydrogen agglomerates were visible in the sample.

Ellis and Evans⁽⁷⁾ compare their experimental results on proton-bombarded

beryllium with studies of proton-bombarded aluminum and helium-bombarded aluminum and beryllium. Evidence is presented that the agglomerates are true hydrogen-filled bubbles. Hydrogen agglomerates are reported to nucleate at grain boundaries with much greater preference than do helium agglomerates; the same comparison holds for hydrogen and helium in aluminum. Results of studies on proton- and helium-bombarded aluminum and beryllium are consistent with the suggestion that as the mobility of the gas is increased it seeks out the more highly preferred points of nucleation for bubble growth.

If it is assumed, as is likely, that bubbles grow by a diffusion process, then it is possible to estimate the diffusion coefficient of hydrogen in beryllium by measuring the rate of bubble growth. An alternative technique to estimate the diffusion coefficient is to measure the rate of depletion of bubbles from the matrix surrounding sites of preferred growth, such as grain boundaries. An example of this is shown in Fig. 12, where the grain boundary near the center of the figure is depleted of bubbles. At longer annealing times, large bubbles are formed in the matrix at distances more remote from grain boundaries (see Fig. 13). In these instances, the depleted zone is equivalent to one-half the inter-agglomerate distance. The absence of bubbles after annealing at 1050°C for one hour may be taken as evidence that hydrogen was able to diffuse from the center of grains to grain boundaries. The depleted zone may then be taken as one-half the mean grain diameter.

Observations made on samples annealed at 750, 850, 900 and 1050°C for various lengths of time are summarized in Table V. The third column gives the lengths of the depleted zones. Estimates of the diffusion coefficient D , given in the last column, are based on the simplified diffusion equation

$$D \sim \frac{x^2}{t}$$

where x is the length of the depleted zone and t is the time⁽¹⁾. The data are not considered sufficiently accurate to estimate an activation energy for diffusion. It is more correct to estimate D as 9×10^{-10} cm²/sec at about 800 to 900°C.

Barnes and Redding⁽⁸⁾, in a study of the agglomeration of helium in alpha-bombarded beryllium, report that bubbles formed after an 8-hour anneal at 700°C indicate that the helium atoms must have diffused about 3×10^{-5} cm. This would indicate a diffusion coefficient of helium in beryllium of the order of 2×10^{-15} cm²/sec at 700°C. That the diffusion coefficient of helium in beryllium is much smaller than that of hydrogen in beryllium is corroborated by the qualitative observations of Ellis and Evans.⁽⁷⁾

V. OXYGEN

In order to determine the solubility and diffusion of oxygen in beryllium an analytical technique is required which is capable of measuring the concentration of oxygen in beryllium at levels below and up to the solubility limit. On the basis of estimates derived from existing analytical techniques, the solubility of oxygen in beryllium is believed to be between 20 and 200 ppm. With the possible exception of activation analysis there is no analytical technique available to determine

oxygen in beryllium at this concentration level.* Furthermore, in order to successfully measure the diffusion of oxygen in beryllium it is necessary that material of lower than saturation concentration be available.

It is not known whether such material currently exists. Therefore, until such time as analytical techniques for the determination of oxygen in beryllium in lower concentration become available, it is not feasible to obtain data regarding the solubility and diffusion of oxygen in beryllium.

* A current program at Texas Nuclear Corporation sponsored by ASD⁽⁹⁾ is studying the determination of oxygen in beryllium by neutron activation analysis.

VI. TABLES AND FIGURES

TABLE I

Nitrogen-Beryllium Alloys

Specimen No.	Nitrogen Content (ppm)	Carbon Content (ppm)	Thermal History	Nitride Present
3A	16	-	As cast	No
23A	36	-	As cast	No
4A	48	-	As cast	No
			As cast + 1000°C - 8 hrs	No
			As cast + 1000°C - 56 hrs	No
			As cast + 1000°C - 56 hrs + 800°C - 196 hrs	No
			As cast + 1000°C - 56 hrs + 500°C - 196 hrs	No
22A	73	-	As cast	Yes
			As cast + 1000°C - 8 hrs	Yes
			As cast + 1000°C - 56 hrs	Yes
			As cast + 1000°C - 56 hrs + 500°C - 196 hrs	Yes
6A	100	370	As cast	Yes
			As cast + 1000°C - 8 hrs	Yes
			As cast + 1000°C - 56 hrs	Yes
			As cast + 1000°C - 56 hrs + 800°C - 196 hrs	Yes
			Slow cooled (4°C/min) from 1340°C	Yes
20A	111	-	As cast	Yes
11A	600	650	As cast	Yes
			As cast + 1000°C - 8 hrs	Yes
			As cast + 1000°C - 56 hrs	Yes
			As cast + 1000°C - 56 hrs + 800°C - 196 hrs	Yes
			Slow cooled (4°C/min) from 1350°C	Yes
13A	2,500	45	As cast	Yes
12A	3,125	-	As cast	Yes
17A	10,000	-	As cast	Yes

TABLE II

Thermal Analysis of Nitrogen-Beryllium Alloys

Accepted values for pure Be $\alpha \leftrightarrow \beta$ 1265°C
 $\beta \leftrightarrow \text{Liquid}$ 1283°C

(6A) Be + 100 ppm N + 370 ppm C	Heating: arrest, 1254-1258°C arrest, 1281-1283°C Cooling: arrest, 1278-1276°C arrest, 1258-1254°C
(11A) Be + 600 ppm N + 650 ppm C	Heating: arrest, 1250-1256°C arrest, 1267-1272°C Cooling: arrest, 1264-1260°C arrest, 1247-1243°C
(13A) Be + 2500 ppm N + 45 ppm C	Heating: arrest, } 1152-1251°C arrest, } Cooling: arrest, 1249-1235°C arrest, 1222-1216°C
(12A) Be + 3125 ppm N	Heating: arrest, } 1280-1360°C arrest, } Cooling: arrest, 1259-1248°C arrest, 1235-1230°C

TABLE III

Nitrogen Concentration in Be-Be₃N₂ Couple
after 17 Days at 1025°C

Distance into Metal (mils)	Nitrogen Concentration (ppm)*	
	Side I	Side II
0 - 3	122	1946
3 - 6	63	(sample lost)
6 - 9	55	87
9 - 12	47	41
12 - 15	41	not detected
15 - 18	41	40
18 - 21	28	16
21 - 24	not detected	not detected

* All answers are ± 7 ppm.

TABLE IV

Typical Analysis of Distilled Beryllium

Impurity	Concentration (ppm)
Fe	3
Ni	2
Cr	1
Mn	5
Si	12
Al	20
Cu	5
N	5
BeO	<300

TABLE V

Estimation* of the Diffusion Coefficient of Hydrogen in Beryllium

Temp (°C)	Time (sec)	Depleted Zone (cm)	Diffusion Coefficient (cm ² /sec)
750	3600	8×10^{-4}	1.8×10^{-10}
850	900	1.0×10^{-3}	1.1×10^{-9}
850	3600	1.6×10^{-3}	6.9×10^{-10}
900	900	1.0×10^{-3}	1.1×10^{-9}
900	2100	1.4×10^{-3}	9.5×10^{-10}
900	3600	1.6×10^{-3}	6.9×10^{-10}
900	7200	2.0×10^{-3}	5.6×10^{-10}
1050	3600	5×10^{-3}	6.9×10^{-9}

* Based on $D = \frac{x^2}{t}$

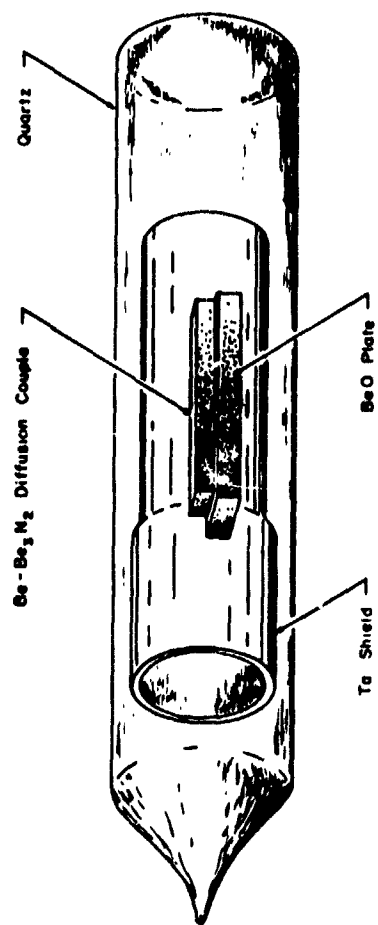


Fig. 1 - Tube used to anneal Be-Be₃N₂ diffusion couple.
Drawing No. RA-2269.

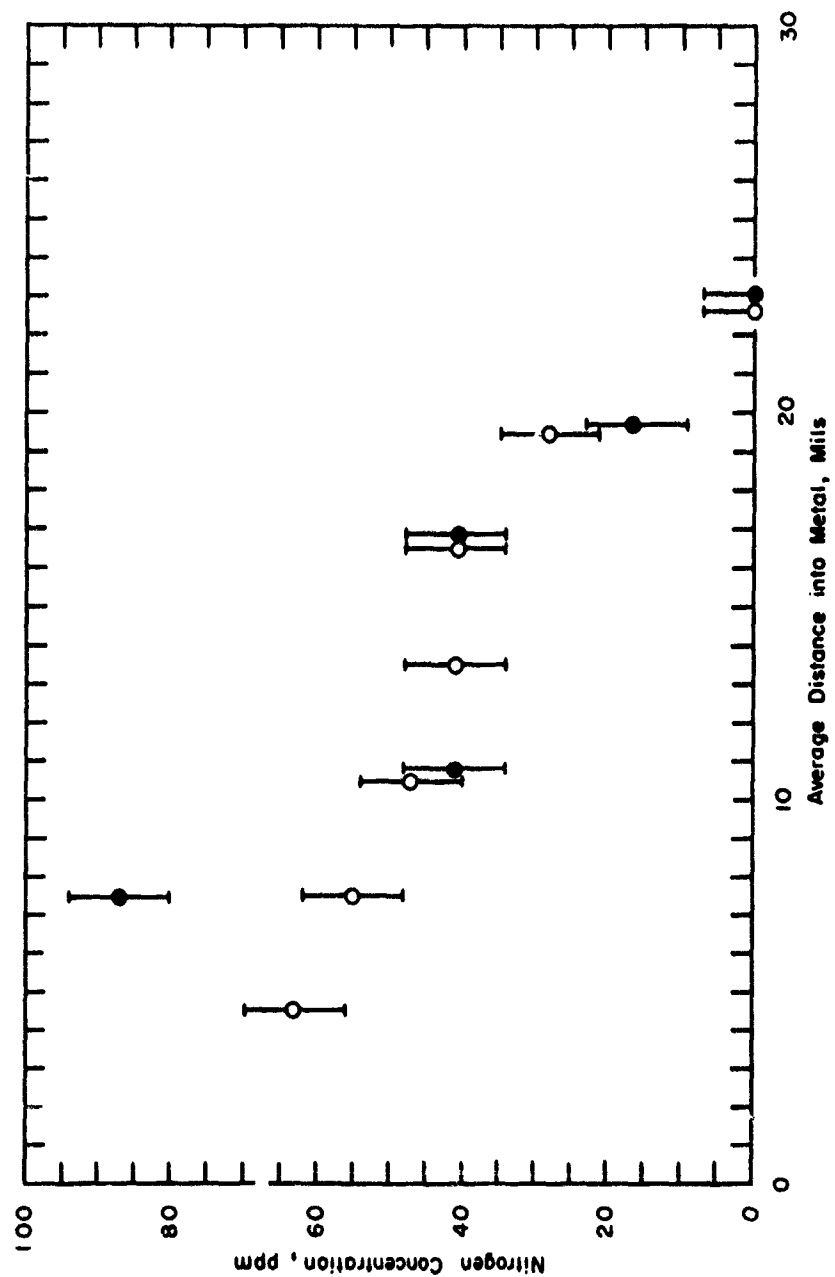


Fig. 2 - Nitrogen concentration gradient in Be-Be₃N₂ diffusion couple after annealing for 17 days at 1025°C. Drawing No. RA-2268

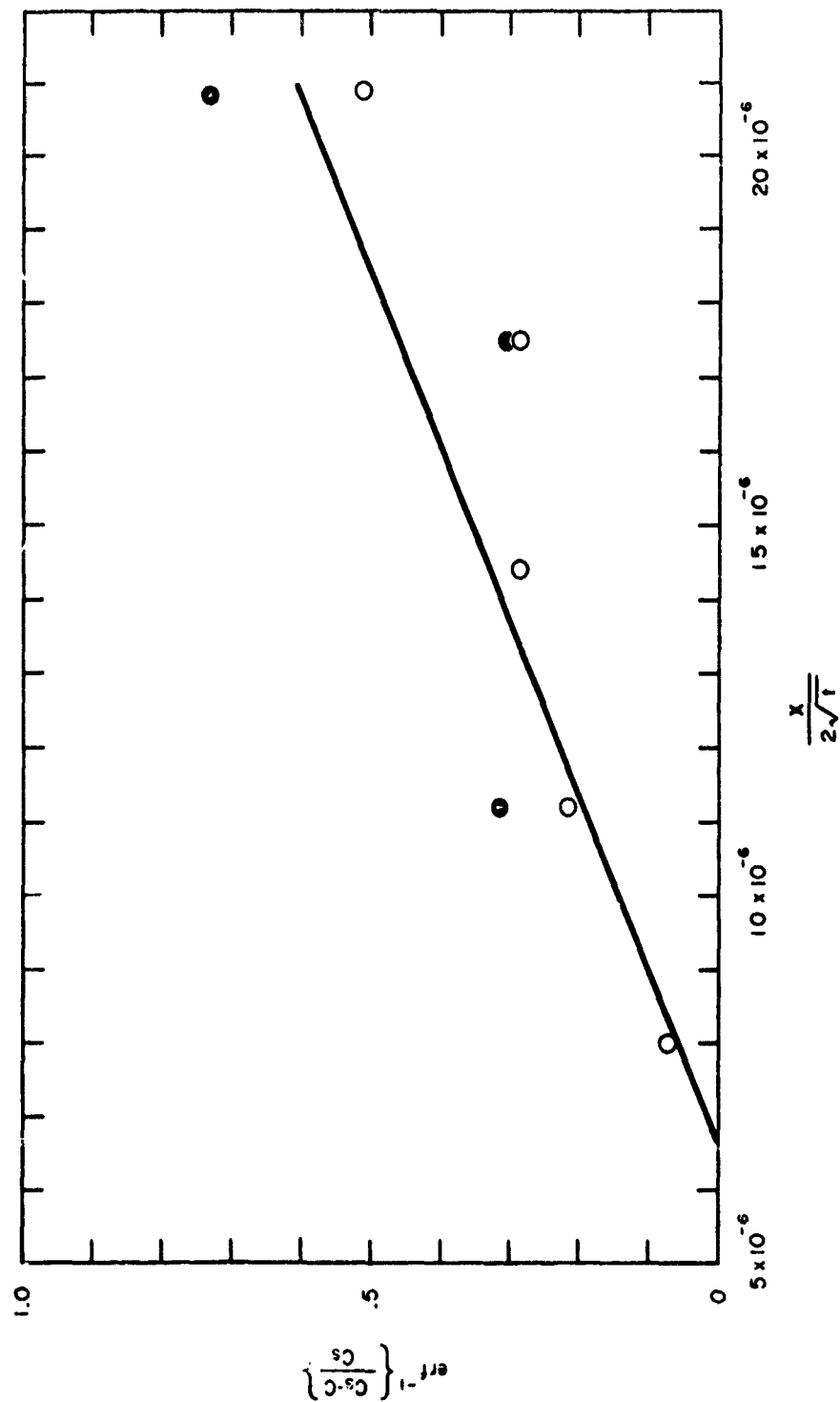


Fig. 3 - Plot used to evaluate the diffusion coefficient of nitrogen in beryllium.
Drawing No. RA-2267.

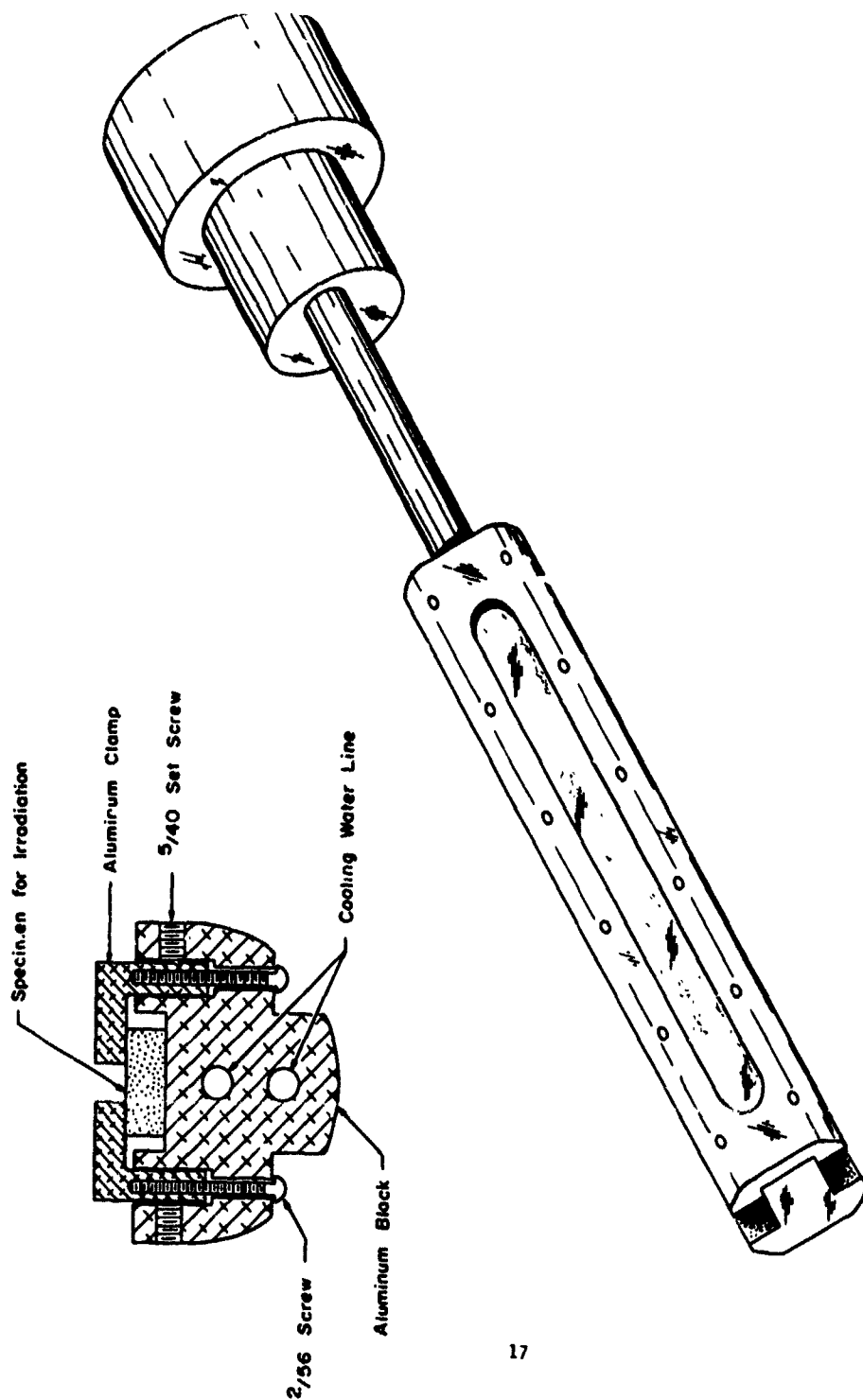
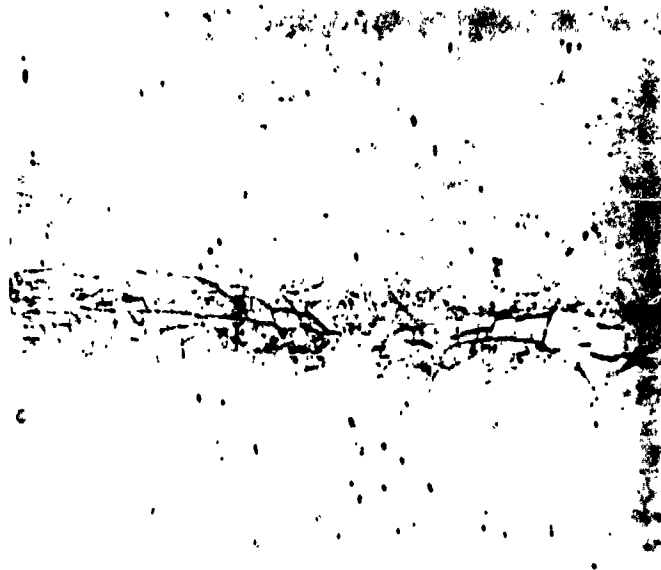


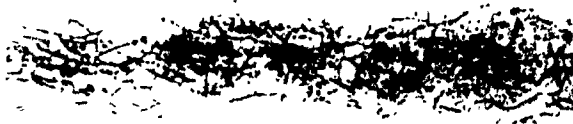
Fig. 4 - Specimen holder for proton bombardment. Drawing No. RB-1133.



500X; Bt. Lt.

B445

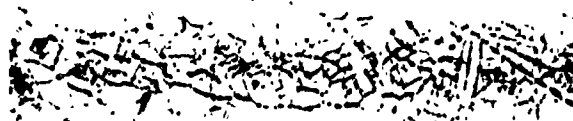
Fig. 5 - Proton bombarded to 170 micro-ampere-hours;
annealed for 1 hour at 350°C.



500X; Rt. Lt.

B446

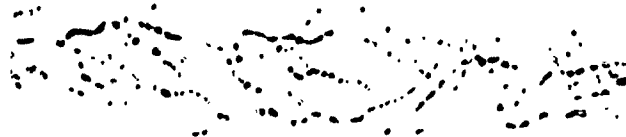
Fig. 6 - Proton bombarded to 170 micro-ampere-hours; annealed for 1 hour at 450°C.



500X; Rt. Lt.

B447

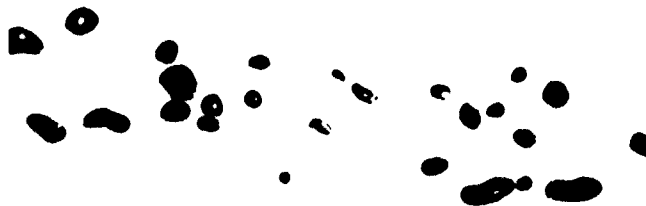
Fig. 7 - Proton bombarded to 170 micro-ampere-hours; annealed for 1 hour at 550°C.



500X; Bt. Lt.

B449-3

Fig. 8 - Proton bombarded to 170 micro-ampere-hours;
annealed for 1 hour at 700°C.



500X; Bt. Lt.

B-452b

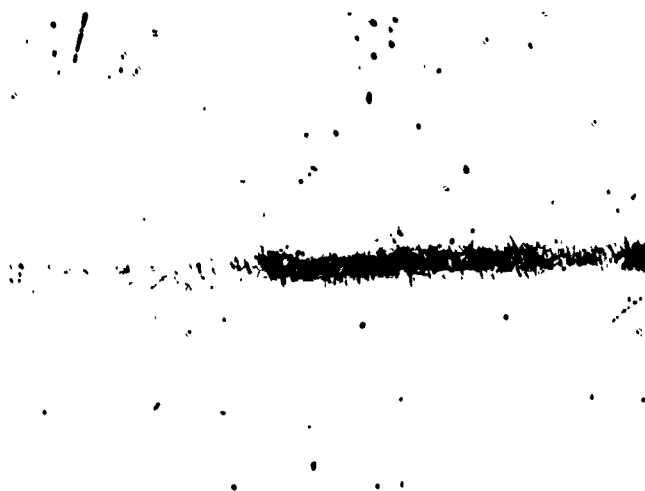
Fig. 9 - Proton bombarded to 170 micro-ampere-hours;
annealed for 1 hour at 900°C.



100X; Polarized

B-452a

Fig. 10 - Proton bombarded to 170 micro-ampere-hours; annealed for 1 hour at 900°C. Hydrogen agglomerates are shown to preferentially migrate to grain boundaries.



100X; Bt. Lt.

B-453-2c

Fig. 11 - Proton bombarded to 17 micro-ampere-hours (right side) and 1.7 micro-ampere-hours (left side); annealed 1 hour at 600°C.



500X; Bt. Lt.

B-467-4b

Fig. 12 - Proton bombarded 170 micro-ampere-hours; annealed for 15 minutes at 850°C. Zone depleted of hydrogen bubbles near grain boundaries is shown.



500x, Et. Lt.

B-463-1a

Fig. 13 - Proton bombarded 170 micro-ampere-hours; annealed for 2 hours at 900°C. Zones depleted of hydrogen bubbles between large agglomerates are shown.

VII. REFERENCES

1. L. S. Darken, in Atom Movements, American Society of Metals, Cleveland, Ohio, (1951).
2. E. A. Gulbransen and K. F. Andrew, J. Electrochem. Soc., 101, 566 (1954).
3. P. Cotterill, R. E. Goosey and A. J. Martin, Paper No. 38, presented at the Institute of Metals, Conference on the Metallurgy of Beryllium, London, England, October 16-18, 1961.
4. J. F. Lemmons and W. B. Lewis, "Predicted Structure and Density of Beryllium Hydride", USAEC Report LA-1659 (1953).
5. G. D. Barbaras, C. Dillard, A. E. Finhold, T. Wartik, K. E. Wilzbach and H. I. Schlesinger, J. Am. Chem. Soc., 73, 4585 (1951).
6. J. P. Pemsler, S. H. Gelles, E. D. Levine and A. R. Kaufmann, "The Purification of Beryllium by Distillation", Paper No. 12 presented at the Institute of Metals, Conference on the Metallurgy of Beryllium, London, England, October 16-18, 1961.
7. C. E. Ellis and W. Evans, "The Behavior of Hydrogen in Beryllium," AECL Report AECL-1347.
8. R. S. Barnes and G. B. Redding, J. Nuclear Energy, Part A: Reactor Science, 10, 32 (1959).

APPENDIX

Calculation of Hydrogen Content of Proton-Bombarded Specimens

The concentration of hydrogen generated in the hydrogen-rich core of the beryllium specimen was calculated by estimating the resulting core volume and the proton beam power (beam current x time). It was assumed that hydrogen was uniformly generated throughout the core.

The volume of the hydrogen-rich core was:

$$11 \text{ cm long} \times 0.9 \text{ cm wide} \times 0.004 \text{ cm thick} = 0.040 \text{ cm}^3.$$

The hydrogen concentration resulting from the 1.7 microamp-hr proton bombardment was determined as follows:

$$\begin{aligned} \text{No. of protons} &= 6.2 \times 10^{12} \text{ protons/sec} (1 \mu\text{-amp}) \times 3600 \text{ sec (1 hr)} \times 1.7 \\ &(\mu\text{amp-hrs}) = 3.7 \times 10^{16} \text{ protons.} \end{aligned}$$

$$\begin{aligned} \text{No. of atoms in the hydrogen-rich volume} &= \frac{V}{V} \times \rho \times \frac{N_0}{M} = 4.9 \times 10^{21} \text{ atoms} \\ \text{where } V &= \text{volume, } 0.040 \text{ cm}^3 \end{aligned}$$

$$\rho = \text{density of Be, } 1.85 \text{ g/cm}^3$$

$$N_0 = \text{Avogadro's number, } 6 \times 10^{23} \text{ atoms/gram-mol}$$

$$M = \text{atomic weight of Be, } 9.013$$

a/o H in hydrogen-rich core -

$$\frac{3.7 \times 10^{16} \text{ protons} \times 100}{4.9 \times 10^{21} \text{ atoms}} = 7.5 \times 10^{-4} \text{ a/o or } 0.00075 \text{ a/o.}$$

Similarly, the concentrations from the 17 and 170 microamp-hr bombardments are 0.0075 a/o and 0.07 a/o respectively.

Aeronautical Systems Division, Dir/Materials and Processes, Physics Laboratory, Wright-Patterson AFB, Ohio.
Rpt No ASD-TDR-62-1018. SOLUBILITY AND DIFFUSION OF GASES IN BERYLLIUM Final report, Feb 63. 25p. incl illus., tables, 6 refs.

Unclassified Report

Results of an experimental program to determine the solubility and diffusion rate of nitrogen, hydrogen, and oxygen in beryllium are reported. The solubility of nitrogen in beryllium at 1000°C is estimated to be about 60 ppm; this value appears to be temperature independent. The results of nitrogen diffusion experiments are considered tentative. The solubility of hydrogen in beryllium is believed to be very small. Measurement of the growth characteristics of hydrogen bubbles formed in beryllium by proton bombardment indicate a value for the diffusion coefficient of hydrogen in beryllium of $9 \times 10^{-10} \text{ cm}^2/\text{sec}$ at 850°C. Due to limitations of chemical analysis, no new data concerning the beryllium-oxygen system was obtained.

(over)

1. Gas diffusion
2. Beryllium
3. AFSC Project 7360, Task 736005
- II. Contract AF 33 (616)-7405
- III. Nuclear Metals, Inc.
- IV. Concord, Mass.
- V. J. P. Fensler, et al.
- VI. Aval fr OTS In ASTIA collection

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