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RESEARCH ON THE PROBLEM OF
DUCTILITY IN BERYLLIUM

By

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I. ABSTRACT

The rate of corrosion of silver by dry chlorine at 600°C and one atmosphere pressure was determined to be about one-thousandth of an inch in one hundred hours, a figure sufficiently low to make the use of silver apparatus in the halide reduction process entirely feasible. Several models of silver chloride valves were constructed and tested. Difficulties in operation rendered this type valve impractical, and it was decided to control the flow of reactant vapors by adjusting helium pressure. An experiment has been designed and equipment assembled to study the chlorination reaction of beryllium with respect to required flow rates of gases and the nature of the condensate. An induction furnace has been designed and constructed for the zone-refining of commercial grade beryllium, and construction of the electron-beam equipment for ultra-high vacuum zone-refining initiated. It is anticipated that the halide reduction process will be ready for operation by about the middle of February and electron beam apparatus tested by the first of March.

II.   INTRODUCTION

This report describes the progress in the research program on production of ultra-high purity beryllium during the period from October 15, 1957 through January 15, 1958. During this time, certain preliminary experiments have been conducted in connection with the halide reduction process, and apparatus has been constructed for low vacuum (10^{-6} mm. Hg) zone-refining by induction heating. The ultra-vacuum system has been designed and component parts procured, and construction of the electron-beam zone-refining equipment initiated. Also, during this time the safety equipment (hoods and associated ventilation) to eliminate the health hazard connected with the handling of beryllium, has been installed.

In addition to the experimental work, considerable library research has been conducted in the field of ductility and purity of beryllium. Although there is little or no experimental evidence to substantiate the view, it seems to be the consensus of most investigators that the brittleness of beryllium is due to impurities, particularly oxygen. Attempts to correlate degree of brittleness with oxygen content generally failed because, quite likely, of the impossibility of preparing oxygen-free metal.

One of the most interesting observations on ductile beryllium was made by Sloman[1], who, in 1932, published results of research on pure beryllium covering a period of eight years. In the course of his attempts to produce ductile metal, Sloman attempted the evaporation technique which is to be used in the present work. Although his experimental methods may be questioned in the light of present-day knowledge, his results are most interesting. Sloman evaporated beryllium in a poor vacuum (5×10^{-2} mm. Hg) onto a surface of vitreous silica.

Neither of these conditions would lead to an oxygen-free material. Surprisingly enough, however, his product, which consisted of a film one millimeter thick, could be "bent backwards and forwards many times before the effect of cold-working led to fracture". Whether or not Sloman's material was pure beryllium, it appears to have been ductile. This result suggests increased emphasis on evaporation in an ultra-high vacuum (10^{-10} mm. Hg).

III.   EXPERIMENTAL RESULTS

A. Halide Reduction Process:

The halide reduction process for the pro-
duction of ultra-pure beryllium has been described in
detail in the previous progress report No. 1, dated
October 15, 1957. Before the assembly of the equipment
in which the chemical reaction is to be carried out is
accomplished, it was deemed advisable to perform several
preliminary experiments. Certain of these experiments
have suggested changes in detail of the system, although
it remains basically as previously outlined. The necessary
experiments were:

(1)   Study of the Corrosion of
      Silver by Dry Chlorine:

For thermodynamic reasons, it was
earlier decided that the part of the system in which
beryllium chloride was produced and distilled should be
fabricated from pure silver. Inasmuch as data on the
reaction between pure silver and dry chlorine at temper-
atures near 600°C are not available, a preliminary experi-
ment has been conducted to determine the rate of attack.
A specimen of silver sheet was sealed in pyrex and main-
tained at about 600°C in dry chlorine at a pressure of
one atmosphere. The specimen was removed and weighed
after each of several exposures of about forty-two hours.
As would be expected, the rate of increase in weight,
which is interpreted as chlorine pick-up, tended to decrease
with each successive exposure. After approximately four
hundred hours, the mass of the specimen had increased from
0.8856 grams to 1.0887, a change of +0.2031 grams. Assum-
ing the increase to be entirely due to added chlorine,
this means (since the atomic weight of silver is about
three times that of chlorine) that about 0.6000 grams of
silver, or two-thirds of the original amount, has reacted.

In terms of thickness of the corroded layer, the rate of penetration of chloride is somewhat greater than one-thousandth of an inch per hundred hours at a temperature of 600°C and a pressure of one atmosphere of dry chlorine. Since the halide reduction apparatus is to be constructed of silver tubing one-sixteenth of an inch thick and will operate at a low partial pressure of chlorine, it may be assumed that the equipment will resist attack indefinitely as far as the project is concerned.

(2) The Reaction Between Beryllium and Chlorine:

Thermodynamic data indicate that beryllium and chlorine should react with some vigor. The only experimental discussion of this reaction which has been found in the literature consists of a report cited by Mellor[2]. In this case, chlorine was passed over "warmed" beryllium and an exothermic reaction observed which caused the mass to glow with white heat. This suggests that considerable care must be taken to control the reaction in order to prevent overheating and melting of the silver reaction chamber. Furthermore, because of the very low specific gravity of beryllium chloride (1.899 gm/cc in the solid state) a study of the condensation of the vapor should be made to insure that the condensate does not form as a fog or snow which will be carried out of the system by the helium carrier gas. Both of these considerations have led to the design and preparation of a preliminary experiment on the production of beryllium chloride. Dry chlorine and purified helium will be introduced into a silver reaction chamber containing beryllium which will initially be heated. The temperature of the chamber will be continuously monitored and kept constant by regulating the partial pressures of chlorine and helium. (If the temperature rises to a dangerous level, the flow of chlorine will be cut off and the system flushed with helium.)

Flow rates of the two gases will be adjusted to provide the desired rate of production of chloride.

The product of the reaction will be condensed in a pyrex chamber in order that the nature of the condensate may be observed visually. If the chloride forms a fog or snow, it will be necessary to design a condensing system which will produce a coherent solid or liquid mass in the chamber.

(3) Design and Construction of Silver Chloride Valves:

The apparatus for the halide reduction process consists of four separate parts: (a) the beryllium chlorination chamber, (b) the beryllium chloride distillation system, (c) the sodium distillation system and (d) the reaction chamber in which beryllium chloride is reduced to metal by sodium vapor. In the original design of the apparatus (see Progress Report No. 1, October 15, 1957), provision was made for isolating each part of the system from the others by means of valves in which changes in the level of molten silver chloride either blocked or permitted the flow of vapors. The changes in level were to be accomplished by magnetically raising and lowering a silver plated iron slug sealed in a reservoir of silver chloride. The design was illustrated in the earlier report.

During the past quarter, several models of a valve have been constructed and tested. Although control of the flow of vapors in such a manner has been shown possible theoretically, a number of technical difficulties have been encountered which render the method impractical. In the first place, the adhesion of silver chloride to silver and the large shrinkage on freezing combine to make it impossible to obtain a vacuum-tight filling in the tube. Vacuum can be maintained only by keeping a molten upper layer on the top of each side of the valve. This difficulty is, in

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itself, insufficient to render the valves unusable since
it is not required to maintain large pressure differ-
entials between parts of the system. It is only necessary
to prevent gross flow of vapors in the wrong direction
and even a moderately leaking valve would suffice. Much
more important was the practical difficulty encountered
in attempting to regulate the level of silver chloride
by means of an iron slug in the reservoir. The large
distance--nearly three inches--through which the slug
would have to be raised made magnetic actuation impossible
and necessitated the introduction of a mechanical lifting
device. This required that the reservoir be open to
the air, an undesirable condition since it introduced a
possibility of the diffusion of oxygen through the imperfect
seal of solid silver chloride. Furthermore, the relatively
high viscosity of molten silver chloride made it difficult
to raise and lower the slug except at temperatures so high
as to weaken the valve assembly. Failure occurred in test
valves when the silver-soldered joints opened.

Because of these technical difficulties it was
decided to redesign the halide reduction system with a
view to eliminating the silver chloride valves. Since,
as was pointed out earlier, there is no need to maintain
pressure differentials between the various systems, all
that is required is a means of preventing flow of vapors
into the wrong part of the system. This can be accomplished
quite satisfactorily by keeping a small positive pressure
of purified helium in each chamber into which entry of
the vapors is not desired. Thus, for example, during the
distillation of beryllium chloride a pressure would be
maintained in the condensing chamber until such time as
the low boiling fractions had been removed. Similarly a
small flow of helium through the chlorination chamber into
the boiling chamber would prevent back flow in that direction.
In the completed assembly of the apparatus, this method of
controlling the flow of vapors will be utilized.

(4)   Distillation of Sodium.

The preparation of distilled sodium
presents no theoretical difficulties and requires no pre-
liminary experiments. Practical considerations have,
however, suggested certain modifications in the apparatus.
Originally, it was planned to fabricate the distillation
and collecting chambers, as well as the connecting tubes,
from molybdenum. However, it has been found to be
extremely difficult to fabricate the desired parts from
molybdenum, and pure nickel has been substituted. Also,
the original design included valves (similar to the
silver chloride valves, except for the utilization of
lithium chloride) between the boiling chamber and the
condensation chamber and between the distillation system
and the reduction chamber. These valves have been
eliminated and flow control will be accomplished by use
of purified helium.

B.   Zone-Refining Process:

(1)   Induction Melting Technique:

Although the ultimate purification of
commercially available beryllium by zone-refining will be
attempted in an ultra-high vacuum of 10^{-10} mm. Hg using
an electron beam as a heat source, it was felt that much
useful information could be obtained by first attempting
the refinement by induction melting in a moderate vacuum
of about 10^{-6} mm. ng. Such factors as size of zone,
rate of travel of the zone, evaporation of the metal,
whether or not impurities are concentrated, etc., can
be studied through simpler experimental methods. To
accomplish this end, an induction zone-melting furnace
has been designed and constructed. This apparatus differs
from those constructed and described by Keck, et al[3] and
by Smith[4] in that it is designed to be operated in the
confined space afforded by the ventilating hood. Further-
more, it has been constructed with a view to as complete

flexibility as possible. Various size coils can be accommodated, specimens of various diameters and lengths up to ten inches can be melted, and the atmosphere can be either a vacuum of 10^{-6} mm. Hg, air or an inert gas. A photograph of the completed equipment is shown in Figure I.

(2) Electron-beam Method:

During the past quarter, the electron beam source and power supply have been designed and fabrication has been initiated. A major simplification has been achieved in the electron gun and the associated focussing arrangement. In the previous report it was suggested that movement of the beam along the length of the beryllium rod would be accomplished by varying the potential across a pair of deflection plates. This was thought to be necessary because motion of the beam by mechanical means would introduce potential sources of leakage between the ultra-vacuum chamber and the outer chamber, which will be at 10^{-6} mm. Hg. Discussions with Dr. Kenneth Shoulders of M.I.T., who has had a great deal of experience with ultra-high vacuum systems and whose basic design is being followed in the present work, revealed that the danger of leakage between the two chambers was of negligible importance. He has found experimentally that an aggregate of as much as one square centimeter of leakage area can be tolerated without affecting the ability of the ion pump to achieve a vacuum of 10^{-10} mm. in the inner chamber. On the basis of this information, it has been decided to move the electron-beam along the specimen by raising and lowering the entire filament and focussing assembly by means of wires passing through ceramic inserts in the top of the ultra-vacuum chamber.

All of the vacuum equipment ordered from outside vendors has been received and is in the process of being assembled.
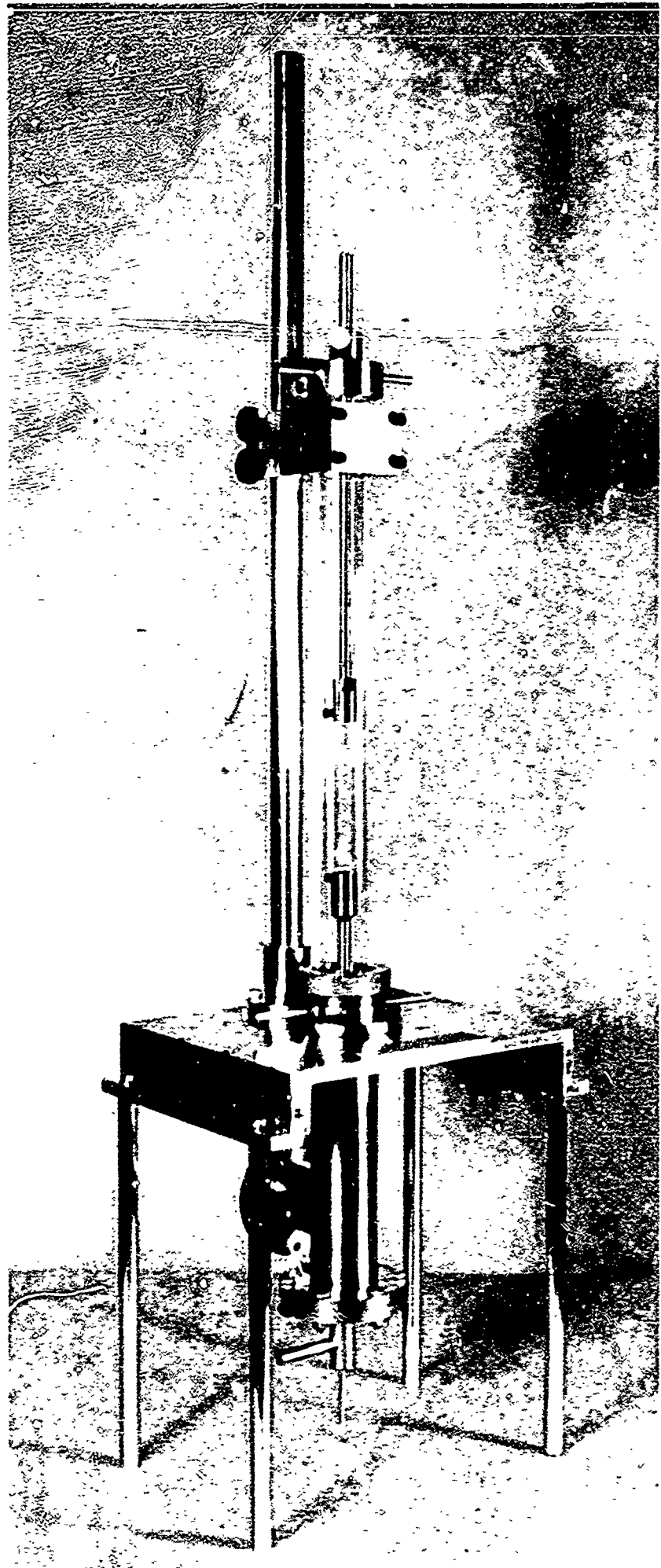
C. Purification by Evaporation:

As was discussed in Progress Report No. 1,
work on evaporation of beryllium in an ultra-vacuum has
been deferred until such time as the vacuum system has
been built and the desired vacuum has been achieved.
The statement by Sloman quoted in the introduction
to this report that beryllium distilled under low vacuum
onto a silica surface is ductile suggests, however, that
this technique may provide the most satisfactory and
simplest answer to the ductility problem. Although the
process hardly lends itself to large production, the
results of Sloman should be confirmed or refuted.

IV. PROGRAM FOR THE THIRD QUARTER

The accomplishments reported to-date have consisted mainly of planning the various attacks to the problem, designing, constructing and procuring component parts for the systems, and performing necessary preliminary experiments. It is anticipated that during the next quarter considerable experimental work will be accomplished on the actual production of beryllium and on the purification of available metal. The following tentative programs for the three processes have been outlined for this period.

A. Halide Reduction Process:

If the results of the preliminary chlorination experiment do not require that extensive changes be made in the equipment for condensing the raw and distilled beryllium chloride, the entire apparatus should be assembled and the first run made by the middle of February. If the reaction proceeds as anticipated and if a deposit of solid metal is obtained in the reaction chamber actual measurement of physical properties may be made by the first of March.

B. Zone-refining Process:

(1) Induction Heating Technique:

It is expected that during the next quarter attempts will be made to zone-refine beryllium. It is anticipated that difficulties will be encountered in melting by induction heating because of the physical nature of beryllium. However, if these are not serious, or can be overcome, actual purification should be accomplished.

(2) Electron-beam Technique:

By the first of March the electron beam apparatus should be in operation in a moderate vacuum (10^{-6} mm. Hg). This preliminary experiment is

necessary since design changes may be required before
it is operated in the ultra-vacuum. Also by this time,
an ultra-high vacuum should have been achieved. If
the first model of the electron gun is satisfactory,
it should be in operation in the ultra-vacuum by the
first of April.

C. Purification by Evaporation

It is expected that equipment for the
evaporation of beryllium in an ultra-vacuum will have
been designed and its construction essentially complete
by the first of April.

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