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BERYLLIUM CORROSION

Final Technical Report to United States Atomic Energy Commission, April 25, 1962 to April 24, 1963

By
D. S. Kneppel

March 24, 1963

Nuclear Metals, Inc.
Concord, Massachusetts

UNITED STATES – EURATOM JOINT RESEARCH AND DEVELOPMENT PROGRAM

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Nuclear Metals, Inc.
West Concord, Massachusetts

Contract No. AT(30-1)-3012
U. S. Atomic Energy Commission

A. R. Kaufmann
Technical Director

FOREWORD

The United States and the European Atomic Energy Community (EURATOM), on May 29 and June 19, 1958, signed an agreement which provides a basis for cooperation in programs for the advancement of the peaceful applications of atomic energy. This agreement, in part, provides for the establishment of a Joint U. S. - Euratom research and development program which is aimed at reactors to be constructed in Europe under the Joint Programs.

The work described in this report represents the Joint U.S.-Euratom effort which is in keeping with the spirit of cooperation in contributing to the common good by the sharing of scientific and technical information and minimizing the duplication of effort by the limited pool of technical talent available in Western Europe and the United States.

P. R. Augustine
Technical Advisor
U. S. Atomic Energy Commission

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ABSTRACT

An investigation of the corrosion behavior of beryllium showed that commercial-purity beryllium will survive in 343°C water without significant attack for prolonged periods. The presence of minute amounts of copper in the water has a deleterious effect on corrosion resistance.

High-purity beryllium exhibits poor corrosion resistance in high temperature water. However, the material can be improved by alloying. Heat-treated alloys containing 0.4 $^{w}/o$ Ni, 0.2 $^{w}/o$ Ni plus 0.2 $^{w}/o$ Fe, or 0.5 $^{w}/o$ Ni plus 0.5 $^{w}/o$ Fe showed good corrosion resistance in 343°C water.

Individual alloy additions to high-purity beryllium of Al, Mg, Mn, Si, Fe, Ni or Cr in amounts comparable to their content in commercial-purity beryllium had no effect in improving the corrosion resistance. The results suggest that a particular combination of elements may be responsible for the fact that the corrosion resistance of commercial purity material is superior to that of high-purity beryllium.

I. SUMMARY

An investigation was made of the factors influencing the corrosion behavior of beryllium in high-temperature water and 400°C steam (1500 psi). Beryllium fabricated from commercial-purity powders (Brush QMV or equivalent) generally showed good corrosion resistance in 343°C water, which, however, did not persist indefinitely. Some samples showed relatively little attack for as long as 162 days before the onset of accelerated corrosion, whereas samples of the same materials in other tests failed in shorter times. This unpredictable behavior appears to be related to the presence of relatively small amounts of copper contamination in the water. There were some indications that elimination of this contamination would significantly extend the corrosion life of certain beryllium materials in 343°C water, possibly to the point where their use in high-temperature water reactors would be feasible from a corrosion standpoint.

Other factors found to have significant effect on the corrosion behavior of beryllium in 343°C water include surface preparation, local boiling, and heat treatment. No evidence was found to indicate any galvanic corrosion between beryllium and oxidized stainless steel, platinum, zirconium, or Zircaloy-2. Correlation of the pH of the water with the corrosion behavior of beryllium was, for the most part, inconclusive. Limited corrosion tests indicated that the factors which caused erratic corrosion behavior in 343°C water were also operative in 315°C water.

The study of the effect of composition on corrosion behavior in 343°C water demonstrated that ultra-high-purity, and even commercial high-purity beryllium materials, regardless of the metallurgical history, invariably corroded catastrophically in exposures of two days or less. The high-purity materials can be made to exhibit good corrosion resistance by alloying. Alloys prepared by hot compacting and heat treating commercial high-purity beryllium powder (Pechiney CR-grade), containing additions of nickel powder (4000 ppm), or nickel plus iron powder (2000 or 5000 ppm of each in two different alloys), have been tested for as long

as 43 days with no sign of attack. Other additions, added individually to high-purity beryllium, which effected no improvement in corrosion resistance even after heat treatment, included Al, Mg, Mn, Si, Fe, Ni (all up to 2000 ppm) and Cr (up to 3000 ppm).

Corrosion tests of different beryllium materials in 400°C steam (1500 psi) indicated a pattern of corrosion behavior similar to that obtained in 343°C water. However, in the materials which initially showed good corrosion resistance in steam, some progression of attack was noted with increased time of exposure. A more rapid breakdown in corrosion resistance occurred after 60 to 100 days in test. Unalloyed beryllium does not appear to be capable of withstanding the corrosive effects of 400°C steam (1500 psi) for indefinite periods of time.

II. INTRODUCTION

The nuclear properties of beryllium make it a very attractive metal for use in atomic reactors. A major deterrent to its use in certain reactor types where the metal would be exposed to high-temperature water has been the problem of corrosion resistance. A previous investigation(1) of the corrosion behavior of beryllium in high-temperature water indicated that the metal showed promising, but unpredictable corrosion resistance in 315°C (600°F) water. Therefore, the objective of the program described in the present report was to investigate intensively the factors influencing the corrosion of beryllium in high-temperature water and steam.

At the outset of the work, it was believed that the corrosion behavior of beryllium was significantly affected by composition. Therefore, initially, the major emphasis of this investigation was directed to a study of compositional variations. The program was planned to consist of two phases. Phase I was to encompass the examination of the corrosion behavior of commercially available beryllium. About 20 samples of beryllium of significantly different purity levels were obtained from the Brush Beryllium Company, the Beryllium Corporation, and General Astrometals, Inc. (representing Pechiney et Cie). These were to be tested in 343°C (650°F) water to yield information on the effect of composition on the corrosion resistance of commercially available beryllium.

In the original planning, Phase II was to encompass studies of very high-purity material and samples prepared by controlled contamination of high-purity material. The high-purity materials to be studied included distilled beryllium, zone-refined beryllium, and super-pure Pechiney flake (SR grade). The results of screening corrosion tests on these high-purity materials were to be compared with the results obtained from the commercial materials of the preceding paragraph. Three possibilities existed: the corrosion behavior of high-purity material would be better, equivalent, or worse than that of commercial-purity material.

If the results showed that the high-purity beryllium exhibited the better corrosion resistance, it could be assumed that deleterious impurities were present in the commercial-purity materials. If no differences in corrosion behavior were observed, it could be concluded that either (a) impurities do not affect the corrosion resistance of beryllium (this situation was considered highly unlikely), or (b) there are combinations of deleterious and beneficial impurities whose effects cancel. In the event that commercial-purity material proved more highly resistant to corrosion than the high-purity materials, it would be evident that the beneficial impurities in commercial material more than offset the effect of any deleterious impurities present.

It was also recognized at the outset of the program that metallurgical factors other than composition would be operative throughout the course of the program. These variables include fabrication methods, surface preparation, heat treatment and grain size. Suitable cognizance was taken of these factors in planning and assessment of the work.

As the work progressed, it became increasingly apparent that the corrosion behavior of high-purity beryllium from all sources was invariably poor. On the other hand, the corrosion resistance of less-pure commercial materials was sometimes good, but the behavior was very erratic. This erratic behavior could not be associated with any effect of composition, but rather appeared to be due to some unknown variations in the test conditions. Therefore, it became necessary to digress to some extent from the original emphasis of the program in order to determine the variations in the test conditions responsible for the erratic corrosion behavior of the less-pure commercial materials. From this work, it was shown that very small amounts of copper contamination in the water caused accelerated corrosion and were responsible for the erratic corrosion behavior.

In the initial work on alloy additions to high-purity beryllium for the purpose of determining the effect of individual impurities on corrosion behavior, compositions were prepared by vacuum melting and casting. However, the above-described results, which showed that commercial-purity beryllium exhibited better corrosion resistance than high-purity material, were obtained on Brush QMV beryllium and equivalent Berylco materials, all of which are powder metallurgy products. Purer powder metallurgy beryllium products (Pechiney CR-grade) were shown to possess poor corrosion behavior.

From these results it was deemed advisable to change the method of alloy preparation to a powder metallurgy approach. Impurity elements present in Brush QMV were added in varying amounts to Pechiney CR powder in an effort to improve its corrosion behavior. This approach allowed a direct comparison with results obtained on the less-pure commercial material which showed good corrosion resistance.

A limited number of steam corrosion tests were also carried out in the program. Various beryllium samples of significantly different purity levels were corrosion tested in steam at $400^{\circ}C$ (1500 psi) and at $650^{\circ}C$ (15 psi).

III. TESTING PROCEDURE AND EVALUATION

A. Autoclaving

The autoclaves, in which the static high-temperature water or steam (1500 psi) corrosion testing was performed, were made of type 347 stainless steel. The volume of these vessels was 2.8 liters (8.25 cm in diameter and 53 cm in depth). Eight autoclaves of essentially identical construction were used interchangeably* for the performance of the corrosion tests in high-temperature water or steam. The test samples were placed on stainless steel (type 304) screen trays (oxidized in high-temperature water or steam prior to use). Distilled water, which was passed through a mixed resin cartridge** just prior to use, was used in all corrosion tests.

1. High-Temperature Water Test

The water charge was 1.2 liters of distilled and deionized water. Corrosion samples were completely covered by water throughout the test. After the autoclave was sealed, it was placed in a heating jacket. When the temperature was about 120°C, a bleed valve was opened and steam allowed to escape for about two minutes. This procedure degassed the water and also flushed the air out of the autoclave. The time required for an autoclave to reach the test temperature of 343°C was about 2-1/2 hours. After removal from the heating jacket upon completion of a test run, cooling of the autoclave to below 100°C took about one hour.

2. Steam (400°C at 1500 psi) Test

The initial procedure for the steam test was the same as for the high-temperature water test, except that the initial water charge was 0.25 liter. When the pressure in the autoclave exceeded 1500 psi as a result of the increase in temperature, the pressure was maintained at about

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* Where additions were made to the water, the same autoclave was used until the particular test was completed. After thorough cleaning, the autoclave was put back into general use.

** Barnstead Bantam 0808 mixed bed, Barnstead Still and Sterilizer Company, Boston, Mass.

1500 psi by bleeding off excess water as steam. Final adjustment of the pressure to 1500 psi was made after the operating temperature of 400°C was reached.

After each corrosion test run, the water was discarded, but in the case of the water test only, the pH was first measured. The autoclave and support trays were thoroughly flushed with tap water and then given a final rinse with distilled water before being used again.

B. Data

1. Weight Gain

After surface preparation (see Section IV-A), samples were cleaned, measured dimensionally, and weighed on an analytical balance. The sides of the corrosion samples, generally rectangular or disc shaped, had surface areas of 0.03 to 0.06 dm^2. Sample weights were of the order of 0.5 to 1.5 grams and were weighed to an accuracy of $\pm$ 0.1 mg.

Weight data for all corrosion samples were obtained as a matter of routine where possible. After a few days in high-temperature water, samples showed weight gains of 20 to 60 mg/dm^2, but showed no further significant weight change until there was visual evidence that sudden breakdown in corrosion resistance had occurred. Weight change data are not particularly useful in assessing corrosion behavior, since it cannot be predicted whether the corrosion products will be retained or lost. In general, weight data are not presented.

2. Visual Observations

Beryllium shows extreme variations in corrosion behavior. In the worst cases, samples after test had completely disintegrated into a white (oxide) powder. Frequently the metal appeared to have been completely converted to oxide, but the samples retained some semblance of their initial shape (see Fig. 1). Less severe attack was evident in some samples where the surface was completely covered with white oxide but the attack had not penetrated very far. In some instances, white oxide occurred in localized areas on the surface.

On the other hand, beryllium samples have been corrosion tested which showed good corrosion resistance for extended periods of time. However, even in these samples some localized pitting attack was apparent, but this attack which developed in the initial stages of the exposure showed no progression. Figure 2 shows a sample corroded in 343°C water for 94 days. The larger white spots* are actually shallow pits containing white oxide. Samples with little attack for long periods of time suddenly showed a breakdown in corrosion resistance. Figure 3 is a sample of hot-pressed beryllium which had shown good corrosion in 343°C for 115 days, but, after an additional 7 days, started to corrode rapidly. Localized spots on the surface were preferentially eroded away leaving very deep pits. Another type of attack in the form of numerous small broken blisters which occurred as a result of localized boiling (see Section IV-H) can be seen in Fig. 4. Generally it has been observed that samples which demonstrated good corrosion for extended times developed some type of localized attack very suddenly.

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* See Section IV-I (Copper Contamination) for discussion of the pinpoint white specks.

IV. RESULTS AND DISCUSSION, UNALLOYED BERYLLIUM

A. Surface Preparation

The surface condition of a sample is an important variable in any corrosion test. In the case of beryllium, improper surface preparation of corrosion specimens leads to premature corrosion failure.

Beryllium, because of its brittle nature, is particularly sensitive to surface damage introduced during fabrication, forming, cutting or machining operations. This sensitivity varies, depending on the metallurgical history of the metal. It is well known that, unless proper precautions are taken to eliminate surface damage of specimens used for tests of mechanical properties, spurious results are obtained.(2) The final step, therefore, in the preparation of beryllium for mechanical tests generally consists of metal removal by chemical or electrochemical means. The large numbers and various types of beryllium corrosion samples anticipated in this program made it imperative that a suitable standard surface preparation be determined for beryllium for corrosion testing.

In order to obtain corrosion samples of convenient size, they were cut on a Di-Met cut-off wheel. It was found that, no matter how carefully the cut was made, surface damage in the form of cracks occurred on cast and extruded metal. Furthermore, it was found that the cracks could only be eliminated when 10 to 12 mils of metal were removed by polishing. Beryllium fabricated from powder showed no evidence of cracks, but this does not preclude the presence of damaged metal.

Removal of damaged metal by etching 10 to 12 mils from the surfaces of the beryllium samples was attempted, using various etchants. Unfortunately, these heavy etches invariably resulted in extensive pitting of the surfaces. The pitted surfaces were judged to be unsuitable for corrosion testing.

In order to obtain some data regarding the value of pre-test etching as a means of improving corrosion behavior, samples were only lightly etched. An etch solution consisting of 1 part HF (conc.), 4 parts HNO_3 (conc.), 15 parts glycerol, and 15 parts H_2O, used at room temperature, removed 0.6 to 0.9 mil of beryllium metal in two minutes. Extruded, vacuum-melted metal showed practically no pitting, and beryllium fabricated from powder exhibited a slight amount of pitting. Nevertheless, as discussed below, the corrosion behavior of samples subjected even to this light etch was poorer than that of samples tested in the as-mechanically-polished condition.

The effect of surface preparation on corrosion behavior was investigated on three types of beryllium: extruded Brush QMV powder, hot-pressed Brush QMV powder, and vacuum-melted extruded Pechiney flake. The vendors' analyses are shown in Table I. One series of samples was polished, varying the depth of metal removal and the final surface finish. An identical series of samples was prepared wherein the samples, after polishing, were etched for two minutes using the solution described above. After etching, the samples were immediately rinsed and then boiled in distilled water. The beaker containing the samples in the hot distilled water was subjected to ultrasonic vibration to ensure complete removal of any surface contamination. The rinsing procedure was repeated to ensure complete removal of any etchant solution trapped in the pores of the surfaces of the samples. All the etched samples were tested in one autoclave and the as-polished samples in another autoclave.

In the first exposure to high-temperature water, the samples were heated to 343°C, held for 15 minutes, and then cooled down. The extruded cast Pechiney samples, in both the etched and as-polished conditions, showed a heavy cracked layer of oxide and were discontinued from further testing. None of the other samples showed any indication of accelerated corrosion, even after an additional 1-3/4 hours' exposure. After a total of 24 hours in 343°C water, all of the etched samples were covered with heavy white corrosion product. By comparison, the identical samples tested in the as-polished condition had not corroded as badly, even in the worst cases, as the etched samples after the same or longer exposure time.

Corrosion test results for samples with varying amounts of metal polished off the surfaces and with different surface finishes are shown in Table II. It is evident that the samples which had been polished to the least depth below the cut surfaces exhibited the greatest amount of local corrosion attack. Any effect of surface finish of as-polished samples on the corrosion behavior is minor in comparison to the effect of the depth of metal removed.

The results obtained indicated that removal of 12 to 14 mils from the surface of samples of hot-pressed or extruded QMV powder generally resulted in samples which showed good corrosion resistance in 343°C water to times indicated (Table II). A standard surface preparation consisting of removal of 12 to 14 mils minimum by polishing followed by surface finishing with 320-grit paper was adopted. Continued corrosion testing of the samples resulted in eventual failure of all the samples (except 19-6) for reasons not connected with surface preparation. These data will be discussed further in connection with the effects of other variables.

B. Effect of Water Temperature

Beryllium fabricated from Brush QMV powder exhibited essentially the same corrosion behavior in 343°C water as in 315°C water. In a previous investigation,(1) some beryllium samples survived 140 to 160 days before the onset of accelerated attack in 315°C water. The same or similar samples corrosion tested in the present program in 343°C water also survived 100 to 160 days before accelerated attack was noted.

An attempt was made to determine quantitatively the difference in corrosion of beryllium in 315 and 343°C water. One set consisting of different samples of extruded QMV powder was tested in 315°C water, and a duplicate set was tested in 343°C water. The samples in 315°C water showed indications of accelerated attack after 21 days, and failed completely after 37 days. On the other hand, of the samples in 343°C water, only one showed any evidence of accelerated attack after 41 days. As a matter of fact, two out of five of the samples in this series survived 162 days before the onset of accelerated corrosion, yet the same samples in 315°C water disintegrated after 37 days. It would appear that the conditions responsible for the erratic corrosion behavior of these beryllium samples are operative at both these test temperatures.

Most beryllium samples other than those fabricated from powder failed catastrophically in water at 343°C in 24 hours or less. In some cases, failure occurred when the autoclave was heated to temperature and then cooled down. This would indicate that attack had started at some lower temperature. No attempt was made in this investigation to determine whether there exists a critical temperature below which no catastrophic attack will occur, regardless of the type of beryllium sample. There has been some work(3) on the corrosion of beryllium to indicate that attack in 274°C water was noticeably less severe than in 315°C water.

The water test temperature in this work has been standardized at 343°C. The higher test temperature was chosen so that differences in corrosion resistance between various samples could be detected after shorter exposure times. However, it became evident that, in spite of the higher water temperature, samples were still capable of surviving 160 days or more.

C. Steam Corrosion

1. 400°C at 1500 psi

The corrosion resistance of various beryllium samples was investigated in 400°C steam at 1500 psi pressure. The results indicate that the corrosion behavior, in tests up to 48 days, is comparable to the corrosion behavior in 343°C water. Samples which behaved poorly in 343°C water also failed in 400°C steam.

Samples obtained from beryllium fabricated directly from powders initially showed good corrosion resistance in 400°C steam. At the outset, arrested local attack of the same type which occurred in water corrosion was noted; however, the attack appeared to progress with longer exposure times. Weight gains in 400°C steam were generally somewhat lower than in 343°C water. After exposures for prolonged times, breakdown of corrosion resistance occurred in the form of localized blisters which broke open (see Fig. 5). The types of samples tested and the times to breakdown in corrosion resistance are shown in Table III. Analyses of the beryllium materials are shown in Tables I and IV as indicated in Table III.

2. 650°C Steam at Atmospheric Pressure

Beryllium samples with varying metallurgical histories were exposed in a quartz apparatus to 650°C flowing steam at atmospheric pressure for relatively short times in order to observe the initiation of corrosion attack and possibly gain an insight into the mechanism of corrosion. Data are presented in Table V. In most cases, the initiation of attack in the form of blistering was observed after a 2-hour exposure. Some samples, however, required additional exposure before they exhibited visual evidence of attack. A cast and extruded sample of Pechiney SR-grade flake showed no visual evidence of attack even after 500 hours in 650°C steam. In addition, the sample showed a neglibible weight change. All the samples fabricated from powder developed tiny broken blisters in 2 hours' exposure which completely covered all surfaces, while cast beryllium samples showed relatively little blistering. The higher purity cast samples appeared to show the least amount of attack. This was in direct opposition to the corrosion behavior in high-temperature water or even 400°C steam at 1500 psi, where the less pure materials fabricated from powder exhibited the best corrosion resistance. Thus, the 650°C steam atmospheric pressure test cannot be used as a substitute accelerated test for high-temperature water corrosion.

D. Effect of Heat Treatment

1. Aging

Investigators(4) have found significant variation in the room temperature mechanical properties of beryllium after various aging treatments. Electron microbeam probe studies indicate that iron segregates to the grain boundaries during aging; a precipitation phenomenon, and therefore, may explain the alteration in mechanical properties. Similarly, aging might have a significant effect on the corrosion resistance of beryllium.

Using the same base material, extruded QMV powder (see Table I for analysis), a series of samples were prepared with different aging treatments. All surfaces of the samples were initially polished to remove about 12 mils of metal per surface. In addition, all of the heat-treated samples were polished to remove the oxide film formed on the surface as a result of quenching into water. The descriptions of the heat treatments and results of corrosion testing in 343°C water for a three-day period are shown in Table VI. Duplicate samples for each condition were corrosion tested. The conclusions which can be drawn from these data are questionable in view of the unexpected poor corrosion resistance shown by the as-extruded material, which, in previous tests, had shown relatively good corrosion resistance. Nevertheless, it seemed significant that the solutionized samples which were not aged failed catastrophically, while the samples aged at 500°C, though showing some attack, were nevertheless much superior as compared to those in the as-solutionized condition. The solutionized samples aged at 700°C for 24 hours (a heat treatment which results in overaging(4)) also showed poor corrosion resistance, but were still relatively better than the as-solutionized samples.

In an attempt to confirm the preceding results, another series of samples was prepared to determine whether aging of beryllium had any effect on its corrosion behavior. The material in this test was extruded QMV -325 mesh powder (see Table IV for analysis) which had shown good corrosion resistance in 315°C (600°F) water for 160 days in a previous program.(1) Duplicate samples of each heat treatment were corroded in 343°C water. The heat treatments and corrosion results are shown in Table VII.

The as-extruded sample was not tested as part of this series of samples. Therefore, a positive assessment of the effects of heat treatment on corrosion resistance cannot be made because subsequent findings have shown that variables in the testing conditions cause erratic behavior. There is some indication in the data in Table VI as there is in Table VII, that solutionizing samples at 1100°C for one hour and then water quenching is particularly detrimental to the corrosion resistance.

2. Preoxidation

Attempts were made to determine whether the corrosion behavior of beryllium could be improved by preforming an oxide film on beryllium which would then serve to better protect the metal from the corrosive effect of high-temperature water. Samples of hot-pressed Brush QMV powder (Table I), extruded Brush QMV -325 mesh powder (Table IV), and the Pechiney samples listed* in Table VIII were heated in oxygen at 550°C for 96 hours. The samples showed no significant weight change. Duplicate control samples of these same materials were sealed in evacuated quartz capsules and given the same heat treatment. All of the Pechiney samples heated in oxygen failed after a one-day exposure to 343°C water, in a manner similar to that shown in Fig. 2. In the water corrosion test of the Pechiney control samples, the autoclave was heated only to 343°C and then cooled, since rapid failure, which in fact occurred, was expected. The preoxidized Brush QMV samples and the Brush QMV controls all showed attack after a total of four days in 343°C water. It is evident that preoxidizing had no significant effect in improving the corrosion resistance on any of the beryllium samples tested.

In another attempt to form an oxide film on beryllium which would protect the material from corroding in high-temperature water, samples of Pechiney grades CR and SR flake, which had been cast and extruded, were exposed to 650°C steam at one atmosphere for a two-hour period. The samples showed no appreciable weight gain or visual evidence of attack as a result of this treatment. Corrosion in 343°C water for one day caused complete disintegration of the samples. It is apparent that the prior exposure to the 650°C steam had no significant inhibiting effect on the corrosion behavior in 343°C water.

E. Galvanic Coupling

In the initial phases of this investigation, the possibility of galvanic corrosion of beryllium in contact with stainless steel was considered. A limited number of tests were made where beryllium samples were supported on synthetic sapphire rods. No improvement was noted in the corrosion resistance of those samples which had shown previous failure when tested resting on oxidized stainless steel screening. Furthermore, there was some evidence of attack at the points of contact with the synthetic sapphire rods, in samples which showed good initial corrosion resistance, so that this method of electrically insulating samples during corrosion

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* The extruded SR-grade flake with the exception of Sample No. 1, was not included because of the high chloride content.

testing may lead to increased attack. At the time, it was judged that any possible effect of galvanic action was minor compared to the effect of corrosion behavior due to metallurgical history and composition. Thus for survey purposes, it was expedient to continue corrosion testing with the beryllium samples in contact with oxidized stainless steel screens.

Since the possibility still exists, however, that galvanic action may be responsible for the erratic behavior of beryllium samples which show promising corrosion resistance, the following test was made. Two rectangular samples of hot-pressed QMV powder, the same as used in previous tests, were clamped between stainless steel blocks with freshly abraded surfaces. After a day's exposure in 343°C water, all of the surfaces not in contact with the stainless steel appeared normal. The two surfaces of one sample in contact with stainless steel showed a slightly increased amount of localized attack. One surface of the other sample in contact with the stainless steel showed a heavy oxide layer. This test is a much more severe condition for galvanic coupling, since the samples were positively clamped to fresh stainless steel surfaces, whereas in normal corrosion tests the samples merely rest on oxidized stainless steel screening. The fact that one surface of the beryllium corroded badly makes galvanic corrosion still a possibility, but on the other hand, this might be the result of some type of crevice corrosion due to limited access of the water to this surface.

In another test, beryllium samples were supported in platinum wire baskets and exposed for three days in 343°C water. The samples showed no evidences of attack, except for an occasional small white oxide spot near the point where the platinum wire contacted the beryllium. The same effects were noted when beryllium samples were supported in oxidized and non-oxidized zirconium wire baskets. Beryllium samples lightly clamped between freshly abraded surfaces of Zircaloy-2 showed no evidences of any attack.

The results of these tests have not completely eliminated the possibility that accelerated corrosion may be caused by galvanic action between beryllium and stainless steel. On the other hand, it cannot be concluded that this type of galvanic action in itself is responsible for the erratic breakdown of the corrosion resistance of beryllium.

F. Effect of Metal Purity

In order to establish any possible trends in the effect of metal purity on corrosion behavior, corrosion tests were run using commercially available samples from the three major suppliers of beryllium: Brush Beryllium Company, Beryllium Corporation, and General Astrometals, representing the Pechiney Company. In addition, beryllium purified by distillation and/or zone refining* was corrosion tested. Table IX compares typical analyses of the various beryllium materials.

1. Brush Beryllium and Beryllium Corporation Compacts

Four Brush Beryllium compacts, and five Berylco beryllium compacts of different chemical compositions, (analyses in Table X) were canned in previously outgassed (1065°C) mild steel. The cans were evacuated and outgassed at 482°C before sealing. The billets were heated to 982°C and then extruded at a reduction ratio of 16:1. The steel was pickled off the extruded beryllium rod with nitric acid. Samples cut from the rod (Run 44, Coupons A and B) were polished to remove a minimum of 10 mils from all surfaces. Subsequently, samples for a repeat test were cut (Run 64, Coupons A and B) and 12 to 14 mils removed from all surfaces by polishing. The results of corrosion testing of both sets of samples in 343°C water are shown in Table XI. Both tests showed that extruded Compact 4 (tests 44-4A,B and 64-4A,B) had the worst corrosion resistance. The analysis of the material on which these tests were run (Table X) showed no obvious difference that would account for the poor corrosion behavior. The BeO content was the highest in this group of materials, but on the other hand the samples prepared from the Berylco Compact No. 8, which contained approximately the same amount of BeO, showed good corrosion resistance.

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* Samples of purified beryllium were obtained from programs performed at NMI for the USAEC and USAF.

The results of the corrosion tests are shown in Table XI. In Runs 44 and 64, Brush samples were tested along with the Berylco samples.

There were no obvious differences in analyses among the Berylco samples which could account for the relatively poor corrosion behavior of Compact 6 (Run 64). In addition, Compact 5A (Run 64) showed accelerated attack after a relatively short exposure, whereas the duplicate samples, 5B, still showed no evidence of accelerated attack after 68 days.

In general, the Berylco samples in Run 64 showed better corrosion resistance than the Brush samples. There were no obvious differences in the analyses between the Brush and Berylco samples which could be correlated with the difference in corrosion behavior.

Metallographic examinations were made of the extruded Brush and Berylco compacts to determine if microstructure could be correlated with corrosion behavior. It was thought that form and distribution of iron-rich particles might have an effect on corrosion behavior. Using a technique originated by Lindsay et al(5), mechanically polished samples were dipped into a phosphoric acid solution containing copper ions. Copper tends to preferentially deposit by chemical replacement on iron or iron-rich particles on the surface of beryllium, and these copper-decorated particles become more readily visible. The technique was inconclusive for the purpose of determining any differences among the samples as to the form or distribution of the iron particles; however, the details of the microstructure became visible apparently as a result of etching of the beryllium surface by phosphoric acid.

Figure 6 shows the microstructure of extruded Brush Compact 4 as revealed by the preceding technique of metallographic preparation . Samples of this compact showed the worst corrosion resistance of the entire series of extruded Brush and Berylco compacts (see Table XI). Figure 7, a sample of extruded Berylco Compact 7, shows a somewhat different microstructure. This microstructure was typical of all the extruded Brush and Berylco compacts in Table X. This same microstructure, using the same metallographic preparation, was also found in other extruded QMV materials showing good corrosion resistance. Figure 8 shows a sample of hot-pressed beryllium whose microstructure was different from Figs. 6 and 7, but, nonetheless, this material exhibited good corrosion resistance. Thus, corrosion behavior cannot be predicted on the basis of microstructure. Furthermore, the microstructure presented no clues as to the mechanism of corrosion failures.

2. Pechiney Company Samples

Six types of beryllium samples fabricated by the Pechiney Company were corrosion tested in 343°C water. The history and analyses of the materials are shown in Table VIII. The appearance of the extruded rods indicated that the surfaces had been ground or polished. Duplicate samples were cut from the metal stock and polished lightly before the corrosion test.

An autoclave containing the samples was heated from room temperature to 343°C in about 2 hours and 15 minutes. The autoclave was removed from the heating jacket and cooled to room temperature in about one hour. At the end of this exposure, only the samples of extruded sintered CR-grade and -200 mesh hot-pressed CR-grade powder showed no evidence of attack. All other samples had developed heavy cracked oxide. Re-exposure of the two good materials for one day at temperature resulted in complete disintegration of these samples.

It was evident from this test that the corrosion resistance of all the extruded cast samples was extremely poor. The extruded sintered CR-grade showed somewhat better corrosion resistance than the higher purity SR-grade. It was also apparent that the hot-pressed -200 mesh CR-grade powder showed significantly worse corrosion than samples with comparable metallurgical history but prepared with less pure beryllium.

Additional samples (except extruded SR-grade flake*) were polished, removing 12 to 14 mils per surface. After a 2-day exposure to 343°C, all the samples except the hot-pressed CR-grade powder had completely disintegrated.** The hot-pressed CR-grade powder sample corroded badly, but

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* The extruded SR-grade flake showed a high chloride content, and there was the possibility that the presence of the chloride in the water after disintegration of the sample would cause the other samples to corrode.

** The test was made with boric acid addition to the water (see Section G). Samples of hot-pressed QMV powder showed good corrosion resistance in an identical corrosion test.

did not disintegrate completely. Thus, even with the proper surface preparation, all these materials show poor corrosion resistance to 343°C water.

3. High-Purity Material Prepared by Nuclear Metals, Inc.

Ordinary commercial high-purity beryllium still contains a fair amount of impurities. It was conceivable that further purification of the beryllium might result in improved corrosion resistance. Samples of very high-purity beryllium were made available through the courtesy of the USAEC and the USAF programs which were being currently performed at NMI.

a. Distilled Beryllium

A sample of beryllium (typical analysis shown in Table XII) distilled from vacuum-melted SR-grade flake was polished, etched and repolished to remove surface defects. A four-day exposure to 343°C water resulted in complete conversion of the sample to oxide. In other samples of distilled beryllium with lesser degrees of surface preparation, disintegration of the material occurred in the time that the samples were heated to temperature and cooled.

Samples from the distillate residues were corrosion tested. The concentrations of nonvolatile metallic impurities, such as Fe, Ni, Cr, etc., in the residue are greater by a factor of 3 as compared with the starting metal SR-grade flake. The samples which were heated to temperature and cooled showed the beginning of accelerated corrosion, but it appeared that the distillate residues showed better corrosion resistance than the distilled metal.

b. Zone-Refined Beryllium

Samples of zone-refined beryllium (see Table XIII) were cut from single crystals by spark machining. The samples were lightly hand polished prior to corrosion testing. Disintegration of the samples occurred in the time that the samples had been heated in water to 343°C and cooled down. All indications are that the super-pure beryllium metal has extremely poor corrosion resistance.

c. Fine-Grained Very High Purity Beryllium

All of the very high purity beryllium samples discussed in the preceding paragraphs were either single crystals or relatively coarse-grained metal. In this investigation and in previous work, coarse-grained or single-crystal beryllium invariably showed poor corrosion resistance. In order to eliminate the effect of grain size in comparing the corrosion resistance of very high purity beryllium with the relatively impure metal, samples were fabricated directly from the high-purity powder. The different grades of beryllium powders used in this series of samples are shown in Table XIV.

The Pechiney SR-grade and Brush QMV powders were cold compacted directly into previously outgassed (1065°C) mild steel cans. The NMI distilled metal and the Pechiney vacuum-melted CR-grade flake were broken up in a beryllium mortar and pestle. Each of the two materials was subsequently cold compacted in a beryllium-lined die using a beryllium ram. The uncontaminated compacts were then put into outgassed steel cans. All of the cans were evacuated, outgassed at 540°C, and then sealed. The billets were heated to 900°C and extruded into flats at a reduction ratio of 11:1. After pickling off the steel, samples were cut and all surfaces polished with a minimum removal of 12 mils per surface.

The samples were heated to temperature in 343°C water and cooled. Those of extruded distilled powder and extruded powder of vacuum-melted Pechiney CR-grade flake showed heavy oxide on all surfaces. On the other hand, the Pechiney SR-grade and Brush QMV extruded powder samples showed only light temper films. After a one-day exposure at temperature, the Pechiney SR-grade sample was completely converted to oxide, whereas the Brush QMV sample still showed no sign of attack. It was evident from this test that no significant improvement in the corrosion resistance was obtained in the higher purity materials by refining the grain size. Comparison of the grain sizes of the different materials was not attempted.

G. Effect of pH

The pH of the water, which was routinely measured at the end of all corrosion test runs, varied from a low value of 5 to a high of 10.5. The high value was measured in one case where numerous samples in test had failed catastrophically. In most instances, the pH was in the range of 6.2 to 7.5. Measurement of the distilled deionized water gave essentially a neutral pH of 7 after the water was degassed by boiling. Furthermore, water which had been at 315°C for two days in a stainless-steel autoclave containing no beryllium had a room-temperature pH of 6.0. This evidence that the corrosion of beryllium caused a definite change in the pH of the water prompted an investigation to determine the effect of pH on the corrosion behavior of beryllium.

All the samples used in the following series of tests were cut from a cylinder of hot-pressed Brush QMV powder (see Table I for analyses). Duplicate samples were used in each test, and all samples were polished with the removal of a minimum of 12 to 14 mils from all surfaces.

In two separate autoclave tests, boric acid was added to the water to serve as a buffering agent to maintain a constant pH. At the start of each exposure the concentration of boric acid added to the normal 1.2-liter water charge was 500 ppm. The results are shown in Table XV and are compared to two control tests with no additions to water. The pH of the water was measured after each exposure, and the range of values is shown under the heading "Final pH".

Initially, the boric acid additions to the water appear to have resulted in less localized (pitting) attack on the samples as compared to the control samples. However, in spite of the fact that the initial and final pH of the water showed relatively little variation, the samples with the boric acid addition to the water failed in shorter times than did the samples tested in the normal manner. It will be noted that the pH of the water at the time of failure of both control runs was abnormally low (5.8). This occurrence has been noted a number of times, and the possible significance of this is discussed in Section I, Effect of Water Contamination.

The corrosion behavior of hot-pressed beryllium was studied in a series of tests where the initial pH of the water was varied by small additions of sodium mono- or di-hydrogen phosphate or a combination of both. The sodium mono- or di-hydrogen phosphate act as buffering agents. An attempt was made to keep the phosphate ion concentration the same in all three tests shown in Table XVI, in order to eliminate any possible extraneous effect that this might have on corrosion behavior. However, in the test with sodium di-hydrogen phosphate by itself the amount added had to be decreased because the initial pH was too low when the phosphate ion was added to the water in the same concentration (80 ppm) as the other test runs. It was feared that excessive corrosion of the stainless steel autoclaves would occur where the pH of the water was too low.

The corrosion results in Table XVI appear to indicate that the samples tested in the more alkaline water (higher pH) corroded more rapidly. However, the samples exposed to water with the initial pH of 5.5, which showed good corrosion resistance initially (6 days), failed after an additional 5-day exposure. (The pH of the water in this test had risen to 9.9.)

This series of tests is considered inconclusive in establishing any effect of pH variation on corrosion behavior, for a number of reasons, but chiefly because the length of time to the breakdown in corrosion resistance was not significantly different among the samples tested.

Samples were corrosion tested in an autoclave into which 35 psi pressure of carbon dioxide was introduced when the autoclave was cold. After a six-day exposure the pH of the water was 4.4. Both samples showed areas of heavy raised oxide where the samples had rested on the stainless steel screening trays. In addition, a fair amount of rust or copper-colored deposit was noted on all surfaces of the samples. It was subsequently shown that this deposit was copper, so there is some doubt as to whether it was the presence of copper (see Section I), or the low pH which caused failure.

In another effort to determine whether the initial alkaline condition was detrimental to corrosion resistance, part of the surface of a sample of hot-pressed QMV beryllium was painted with a slurry of aluminum hydroxide which was allowed to air dry before the sample was placed in the autoclave. Another sample of the same material, unpainted, was put into the same autoclave to serve as a control. After a three-day exposure, both samples showed good corrosion resistance; there was no essential difference in their appearance. The aluminum hydroxide had disappeared from the surface of the one sample, and the final pH of the water measured 8.0. The same area of one of the samples was again painted and the samples were put back into test. This procedure was followed for three exposures for a total of 17 days at temperature. The pH of the water after the third test run was 6.9. It was noted that a fair amount of copper-colored specks had been precipitated on the surface of both samples.

The evidence from this test would indicate that beryllium can tolerate moderately alkaline water (pH of about 8) without showing accelerated corrosion. Thus, it is not certain that pH in itself has any major effect on the corrosion behavior of beryllium in high-temperature water. Sample failure has been noted in test runs where the water after the test was mildly acid, neutral or mildly alkaline. On the other hand, samples have also showed no failure when these same water conditions existed at the end of the test runs.

H. Local Boiling

Indications have been obtained that boiling on the surface of beryllium is a contributing factor to erratic corrosion behavior. For the purpose of determining how prior exposure to steam affects the corrosion resistance in water, beryllium samples of hot-pressed QMV powder were exposed to 400°C steam at 1500 psi for four days. A three-day exposure to 343°C water following the steam exposure showed no evidence of any accelerated corrosion. The samples were reloaded in an autoclave for further water testing. When the temperature reached about 320°C, a massive steam leak suddenly developed around the gasket, at which time the autoclave was immediately removed from the heater and cooled down. Examination of the samples showed numerous small broken blisters on all surfaces of the beryllium (see Fig. 4). The type of attack was very similar to that which occurred when beryllium samples were corroded in 400°C steam at 1500 psi (see Fig. 5). The unusual occurrence of a massive leak and the abnormal behavior of the samples appeared to be more than a coincidence. It was assumed that the sudden release of steam pressure due to the leak caused the water to boil and that some of the boiling occurred on the surface of the samples. In some manner, boiling on the surface of the samples resulted in very rapid accelerated attack of the beryllium.

In order to verify this effect of local boiling, duplicate samples of hot-pressed QMV powder were loaded in an autoclave containing 350 ml excess water over the normal water charge of 1200 ml. After the autoclave reached 343°C, this excess water was slowly bled off as steam through the bleed valve at intervals over a 24-hour period. During the time that the steam was being bled, boiling of the water must have occurred in the autoclave. After a five-day exposure of the samples, one sample showed no attack on any surface. The other sample showed heavy white oxide on the top surface and also covering about one-half of the surface area of the sides. The bottom surface of this sample showed no signs of attack other than a normal light temper film. It was especially significant that attack, when it did occur, took place on the top surface where boiling on the surface would most likely occur.

A similar test was made in which 300 ml of water was bled off as steam very rapidly (45 seconds). The pressure and the temperature dropped off very sharply. After 16 hours at temperature, one sample showed white oxide on all surfaces, and the other had white oxide on the top surface only (Fig. 9). The formation of steam bubbles (or boiling) preferentially occurs on any surface; however, the occurrence of boiling on a particular surface is unpredictable. This might account for the difference in corrosion behavior of the two samples in this and the previous test. It can only be assumed that boiling did not occur on the surfaces of the samples where no attack was observed.

Using the same autoclave as in the test in the previous paragraph, and duplicate samples of the same hot-pressed QMV beryllium, a corrosion test was run in the normal fashion. After a 16-hour exposure in 343°C water, one sample showed white oxide on all surfaces and the other no attack at all.

New samples of the same material were tested in the same autoclave, but this time the autoclave was pressurized with argon at room temperature.

After the autoclave was sealed, the autocalve was vacuum pumped through the bleed valve for a period of 10 minutes. This served to eliminate the air in the autoclave and also degassed the water. Tank argon was bled into the autoclave to a pressure of 100 psi and the bleed valve closed. The autoclave was then heated to temperature without further degassing.

Exposure of the samples to 343°C water for 16 hours showed no attack on either of the two samples. Additional exposure of the samples in the autoclave overpressurized with argon for up to 25 days has been obtained with no evidence of accelerated attack. From these series of tests, it seems fairly definite that boiling on the surface of samples in high-temperature water can cause accelerated attack, and this was probably part of the cause of the sometimes erratic corrosion behavior of some beryllium materials. As a precautionary measure, all subsequent corrosion tests have been made in autoclaves with an overpressure of 100 psi of argon (room temperature). Unless otherwise stated, it can be assumed that all tests discussed hereafter were performed in this manner. Tests have been made which indicate that beryllium samples which have invariably shown poor corrosion behavior when tested in the old manner show no improvement in argon-pressurized tests.

I. Effect of Water Contamination

1. Copper Contamination

It was noted that the surface of corrosion samples occasionally showed very fine shiny specks of what appeared to be a rust-colored precipitate. These were not readily detectable at magnifications lower than 25X. No particular significance was attached, initially, to these observations, since these specks were seen both on samples that showed no evidence of accelerated attack and on samples that showed attack. Furthermore, previous experience with similar specks on zirconium exposed in these same stainless steel autoclaves had demonstrated that the specks were iron oxide, and they had no effect on the corrosion behavior of the zirconium samples in test.

A routine analysis by x-ray fluorescence was made on a corrosion sample that showed these fine specks on the surface. Unexpectedly, the analysis showed no evidence of iron, nickel or chromium, but very definite evidence of copper. Subsequently, the presence of copper precipitated on the surface of corroded samples was confirmed by etching a sample in 1:1 nitric acid. No attack of the oxidized beryllium surface was evident, but the shiny specks had disappeared. Analysis of the etchant solution showed that the material removed was copper. Examination of the surface of another corrosion sample was made by an electron microbeam probe. The precipitated specks on the surface were again shown to be copper.

Closer examination of the surfaces of all corroded beryllium samples showed the presence of the adherent copper precipitate which, from visual appearance, was in the metallic form rather than the oxide. Figure 2 is a macrophotograph of the surface of a corroded sample showing the presence of coppery precipitate. The precipitate, because of its shiny nature, appears as very fine white specks uniformly distributed over the surface. Actually, at the magnification at which the picture was taken, it would be difficult to detect the specks on the surface except for the fact that the reflected light from their shiny surfaces makes them more distinct.

As soon as it was evident that copper was precipitating on the surface of beryllium corrosion samples, attempts were made to find and eliminate all possible sources of copper contamination and, in addition, to determine whether, in fact, copper contamination contributed to the erratic corrosion behavior of beryllium. Analysis of the distilled water showed 45 ppb (parts per billion) of copper, but the water prior to use was passed through a mixed resin bed which dropped the copper content down to less than 10 ppb. The distilled deionized water had been used throughout this program right from the start, so that the water was eliminated as the cause of copper contamination.

A source of copper contamination was found in the gaskets used to seal the autoclaves. These gaskets were made of copper which had been electroplated with silver specifically for the purpose of preventing copper contamination of the water. However, it was noted that, because of the repeated opening and closing of the autoclaves, the silver had in some instances peeled away, exposing the copper. The use of these gaskets was immediately discontinued and stainless steel gaskets substituted. In addition, the interior of the stainless steel autoclaves and all the sample support stainless steel screening trays were etched in 1:1 nitric acid-water solution to remove any copper that may have been deposited.

In order to determine whether copper in the water caused accelerated corrosion, a test was made with a solid piece of copper placed in the water with beryllium corrosion samples of hot-pressed QMV powder. After a three-day exposure to 343°C water, the corrosion samples showed only light localized attack which, nevertheless, was more attack than was usual for these same samples tested in the normal manner. The samples showed a relatively heavy precipitate of copper on the surface. The copper piece remained bright. Another four-day exposure showed no change on the beryllium samples or the copper. Further exposure, to give a total of 11 days, showed definite accelerated local attack on the beryllium samples, and the copper showed a flaky black oxide film. The pH of the water at the end of this test run was 5.2, as compared to 6.8 and 6.9 in the previous exposure.

Another test was made where 6 milligrams of copper powder was added to the water charge (1200 ml) before each exposure. The results are shown in Table XVII. Duplicate samples of each beryllium type were tested in each autoclave.

Duplicate samples of the same beryllium materials were tested in an autoclave without any deliberate copper contamination. The autoclave was etched in a 1:1 nitric acid solution and thoroughly rinsed just prior to use. After a seven-day exposure to 343°C water, not one of the six samples tested showed evidence of any attack, whereas by comparison the same samples in the copper-contaminated autoclave all showed at least some localized attack. The samples in the copper-contaminated autoclave showed relatively heavy copper precipitate on the surface. In spite of the precautions taken, the samples in the presumably copper-free autoclave still showed some copper specks on the surface of the samples.

These tests have definitely indicated that copper contamination can cause accelerated attack to occur on samples where previous testing had shown the samples capable of survival for much longer exposures. The data in Table XVII indicate that some beryllium materials are more susceptible to the effects of copper contamination than others. Furthermore, it was evident that samples exposed to copper-contaminated water did not necessarily show immediate catastrophic corrosion, but eventually rapid attack was triggered. This was seen in the first test where samples of hot-pressed beryllium exposed to water containing a solid piece of copper survived seven days with only relatively minor attack. After an additional four days, the samples showed fairly extensive attack, and the pH was an exceptionally low 5.2. Similar occurrences have been noted in previous testing. Samples exposed to 343°C water showed only some arrested localized attack, up to 68 days. After an additional 12 days, the samples showed accelerated attack, and the pH of the water was 5.8. In another case, samples in test suddenly developed accelerated attack after 133 days in test, and the pH was 5.1. In still another test, different samples of beryllium had been exposed for different lengths of time (see Table XVIII). All simultaneously showed a breakdown in corrosion resistance when put back into test in the same autoclave. Again the pH of the water was on the low side (6.4). Re-examination of all the samples showed copper on the surfaces. It was also significant that the pH of the water at the time that failure of the samples occurred was generally lower than normal. The reasons for this were not known. Furthermore, it was not known whether the low pH resulted from the corrosion reaction or the low pH was the cause of the accelerated reaction, but in any case the effect of copper contamination on corrosion behavior appeared to depend in some manner on the pH of the water.

All the evidence indicates that copper contamination was responsible for the breakdown in corrosion resistance of samples which showed only minor arrested attack for as long as 162 days in 343°C water. If this is true, then beryllium should be capable of surviving exposure to 343°C water for much greater lengths of time without accelerated corrosion. Unfortunately, there was insufficient time remaining to amass the exposure times required to obtain final proof. However, there is some evidence for believing that beryllium can survive exposure beyond 162 days without showing accelerated corrosion. A sample of extruded QMV beryllium powder (see Table IV for analysis) had a total exposure of 133 days in 343°C water. The sample showed only some arrested localized pitting. It was at this time that it was realized that copper contamination of the water was occurring, and closer examination of the surface of the sample revealed copper precipitate on the surface. The sample was etched in 1:1 nitric acid solution which, other than removing the copper, appeared to have no effect. The sample was then put back into test for further exposure in an etched autoclave where it was thought that the sources of copper contamination had been eliminated. After an additional eight days in 343°C water, copper was again found on the surface, indicating that a source of copper contamination still remained. However, by etching the samples to remove the copper precipitated on the sample and etching the autoclave before each test run, the sample survived a total of 183 days exposure and still did not show a breakdown in corrosion resistance. This is the only direct proof that has been obtained that indicates that unalloyed beryllium is capable of surviving exposure to 343°C water beyond 162 days.

The substitution of stainless steel gaskets for the silver-plated ones and etching of the autoclaves did not eliminate the precipitation of copper on the beryllium corrosion samples. An analysis of the water for copper after a corrosion test where copper deposited on the samples showed 60 ppb, and the pH of the water was 6.1. Analysis of the water in a different autoclave after a corrosion run showed 130 ppb of copper. The amount of copper dissolved in the water at the test temperature may have been considerably higher.

At the time this report was being written, two other sources of probable copper contamination were discovered. After elimination of these, a corrosion test run was made in which no copper precipitate was detected on the surface of samples after a 7-day exposure. Analysis of the water after the run showed only 10 ppb, which is essentially that of the starting distilled and deionized water used in the test.

2. Other Contamination

When it was discovered that copper contamination was a possible cause of the erratic corrosion behavior, experiments were made to determine whether other contaminations might also be causing erratic behavior.

a. Distilled Beryllium

Tests were made in which pieces of distilled beryllium were exposed in an autoclave containing corrosion samples of beryllium. The purpose was to determine whether excess BeO in the water would affect the corrosion behavior of the beryllium samples.

Distilled beryllium disintegrates rapidly in high-temperature water and since it contains only about 60 ppm of total metallic impurities (see Table XII), a 0.4-gram piece would only introduce about 20 ppb of total metallic impurities into the 1200-ml charge of water in the autoclave. A piece of distilled beryllium after a two-day exposure in 343°C water had disintegrated completely to oxide. The pH of the water at the end of the test was 8.4.

In two separate test runs, 0.3 and 0.45 grams of distilled beryllium as solid pieces were placed into the water along with corrosion samples of hot-pressed QMV beryllium. After each exposure, the oxidized disintegrated distilled beryllium was removed and continuation of the test was made with fresh water and another piece of distilled beryllium. The data shown in Table XIX indicate that there was no detrimental effect resulting from the presence of the BeO in the water.

b. QMV Powder

QMV beryllium powder contained in an oxidized stainless steel cup was put in the water along with two solid corrosion samples of the hot-pressed QMV powder. After a seven-day exposure in 343°C water, the QMV powder showed a fair amount of white oxide, but the metal powder was not by any means entirely consumed. Both of the solid samples were attacked. One sample showed a white oxide layer which had flaked off. The pH of the water was 8.7. There was a distinct possibility that the contamination of the water due to the corrosion of the QMV powder resulted in accelerated attack on the solid beryllium samples.

c. Metallic Contamination

Corrosion tests were made to determine which specific metal contamination of the water would result in accelerated attack. In each case, the metallic impurity was added in powder form to give a concentration of 5 ppm of the metal in the water. Duplicate samples of hot-pressed QMV powder were used in each test. After each exposure, the water was changed, and a new addition of the metal impurity was made to the water.

The results are shown in Table XX. It appears that the copper (oxide), nickel (oxide), iron and manganese additions to the water resulted in increased localized attack on the beryllium samples, whereas the chromium, magnesium and aluminum additions had no effect up to the indicated exposure times.

V. RESULTS AND DISCUSSION - CONTROLLED PURITY BERYLLIUM

A. Experimental Approaches

In the initial planning of this investigation, it was assumed that the composition of beryllium was a major factor in the corrosion behavior. It was known from a previous investigation(1) that commercial-purity (QMV) beryllium showed promising corrosion resistance in high-temperature water, but the behavior was very erratic, and it was considered likely that the erratic corrosion behavior of the commercial-purity beryllium materials was due to compositional effects. It was not known whether the impurities present in the commercial-purity beryllium acted deleteriously or beneficially on the corrosion resistance of the material. Thus, it seemed desirable to attempt to classify individually the major impurity elements in commercial beryllium as to whether they were detrimental or beneficial to the corrosion behavior, and also to determine the effective amounts.

In order to obtain samples for corrosion testing within a reasonable time, it was necessary to start work on alloy preparation at the inception of this investigation. The method initially chosen was to add the alloys to high-purity beryllium by vacuum melting and bottom pouring of the melt into a BeO crucible. It was hoped that this method of casting would result in relatively fine-grained ingots. Grain size would be further reduced by extrusion. Samples of the extruded material would then be corrosion tested for evaluation of the particular addition on corrosion behavior. Alloying additions by melting allowed the use of the relatively high-purity* commercially available Pechiney SR-grade flake beryllium.

As the work progressed in other phases of this investigation, it became apparent that alloy additions made by a powder-metallurgy process would be better suited to obtaining meaningful information on the effects of composition. High-purity beryllium samples, regardless of the methods of fabrication, invariably corroded rapidly. Included in this class of materials

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* Distilled beryllium of significantly higher purity was considered for use, but the cost of the material was prohibitive, even if only one melt was made of each of the major impurities to be investigated.

showing poor corrosion resistance were samples made from Pechiney CR-grade powder. On the other hand, samples prepared from less-pure commercial powders (Brush QMV or equivalent Berylco grade) showed good corrosion resistance. Thus, by small additions of the proper elements to the Pechiney CR-grade powder, it was reasoned that it should be possible to obtain material with corrosion resistance comparable to that of samples prepared from the less-pure QMV powder. It seemed advisable at this time to study the effect of composition by blending small alloy additions with Pechiney CR-grade powder and fabricating by hot-pressing. Previous work (6) had indicated that this technique was capable of producing uniform homogeneous alloys.

B. Extruded Cast Alloys

Four alloys, each containing a nominal 1 $^w/o$ addition of Fe, Ni, Cr or Al to Pechiney SR-grade flake, were prepared by the method of melting and casting. In this initial alloy work, the 1 $^w/o$ alloy level was arbitrarily chosen in the effort to determine the influence of each element on corrosion behavior. Some basis for choosing a 1 $^w/o$ level for exploratory work on the nickel addition was provided by a previous study(1) which showed that an extruded casting of a Be - 0.66 $^w/o$ Ni alloy exhibited good corrosion behavior in 315°C water for 280 days.

An additional alloy containing a 1 $^w/o$ addition of cobalt to commercial purity QMV beryllium was also available for test. This melt was made for the purpose of proving out the melting and casting apparatus (described below) prior to making the four melts with Pechiney grade beryllium.

The apparatus for preparing these alloys is shown in Fig. 10. Castings 1-1/4 inch in diameter weighing from 50 to 75 grams were obtained by bottom pouring. The charge, consisting of 100 grams of SR-grade Pechiney flake (analyses in Table XXI), together with 1 gram of the alloy addition, was loaded into the melting crucible. The system was evacuated and the charge heated by induction to about 1000°C to remove volatile material. Purified argon was then admitted to the system to suppress volatilization of beryllium, and the charge was heated to above the melting point and held in that condition for about 10 minutes. The stopper rod was pulled, and the metal flowed into the BeO catch crucible. An appreciable amount of sintered beryllium adhered to the sides of the crucible and the stopper rod, so the yield was only 50 to 60 grams of alloy. However, after a subsequent modification of the apparatus, in which a poke rod of BeO was used, the yield was substantially increased to 80 to 90 percent. It was noted that the castings contained pipes extending in about three-quarters of the length of the casting.

The castings were sealed in evacuated mild steel cans which had been previously outgassed. The cans were heated to 970°C and extruded at a speed of 65 inches per minute to a flat of 1/8 inch by 1 inch, which constituted an area reduction of 12:1. Breakage of the die prevented extrusion of the 1 $^w/_o$ iron alloy. In view of the results obtained in the subsequent corrosion testing of the other samples, no attempt was made to salvage this alloy. The steel was pickled from the extruded beryllium flats with nitric acid.

Chemical analyses of samples of the nominal 1 $^w/_o$ alloys cut from the front, center and rear of the extruded flats are shown in Table XXII. The nickel alloy shows chemical segregation along the length. The cobalt and chromium alloys showed chemical homogeneity, but it was apparent that some of the alloying element was lost in casting.

Samples for corrosion from the front, center and rear of each extruded alloy were polished to 14 to 38 mils below the extruded surfaces in order to eliminate possible iron contamination due to the extrusion steel can.

The alloy containing 1 $^w/_o$ aluminum addition disintegrated completely to white powder after a four-day exposure in 343°C water. No attempt was made to determine the actual aluminum content of the material, since it was evident that the aluminum addition showed no indication of improving the corrosion resistance.

No discernible attack was observed on the chromium alloy sample after a one-day exposure in 343°C water. After one day, the cobalt alloy samples were completely covered with white oxide, whereas the nickel addition samples showed some light localized attack. The front sample of the nickel alloy also showed a heavy raised line of oxide on one edge. Testing of all of the cobalt alloy samples and testing of the nickel sample fron the front of the extrusion was discontinued at this point.

After seven days of cumulative exposure to 343°C water, accelerated attack of the remaining nickel alloy samples resulted. Heavy lines of spalled oxide parallel to the extrusion direction were visible on the surfaces. The chromium alloy samples still showed no evidence of attack; however, after 14 days of total exposure, the front and middle samples developed the same type of attack as the nickel alloy samples. The mode of attack suggested that inhomogeneity was present in the samples.

A repeat test was made on samples of the nickel and chromium alloys; after a total exposure of 13 days, all samples showed similar attack along the extrusion direction. Metallographic examination of samples transverse to the extrusion direction showed little or no evidence of any type of segregation. However, in the direction parallel to the extrusion axis, the samples showed gross variations in grain size, which were visible in macroexamination. In addition, numerous casting defects were present in the sample.

It was evident that the method of extruding small castings gave unsatisfactory samples, because of uncertainties in obtaining homogeneous (chemical and grain size) material of the desired composition. This was evident from the manner in which the samples corroded, the chemical analyses and, to some extent, macroexamination. Although these difficulties probably could have been overcome by further experimental effort, the melting and casting work was abandoned at this point in favor of the powder metallurgy approach, for reasons discussed previously.

C. Powder Metallurgy Alloys

Twenty-three alloys were prepared by a powder metallurgy method in which the alloying elements were added to -200 mesh Pechiney CR-grade powder. Vendor's analysis of the starting powder is shown in Table XXIII. The amounts of alloying additions are shown in Table XXIV. Binary alloys containing additions of Al, Cr, Mg, Mn, Si or Fe were prepared in which the amount of alloying addition bracketed the amount that these impurities are normally present in Brush QMV amterial. Nickel additions (up to 4000 ppm) were made on the basis of previous work where it had been shown that beryllium alloys containing nickel had good corrosion resistance.(1) Actually, nickel alloy additions would not have been made simply to duplicate QMV beryllium, since the amount present in CR-grade beryllium is about the same as in QMV grade. The combinations of nickel and iron additions were made on the basis of work done by Draley and Ruther(7) where it was shown that the addition of iron to an Al-0.66 w/o Ni alloy was necessary in some cases for good corrosion resistance in high-temperature water.

For comparison purposes, an additional hot-compact was prepared from -200 mesh QMV powder. The vendor's analysis of this material is shown in Table XXIII.

The method of preparing alloys consisted of blending the Pechiney powder with the particular impurity in powder form, followed by hot compaction. This method is described in detail below and is essentially the same as methods previously used successfully for preparation of homogeneous beryllium alloys.(5)

The steps used in the preparation of the alloys were as follows:

1. Approximately 40 grams of beryllium powder and the alloy addition, also in powder form, were blended by rolling with Teflon cubes for 24 hours.
2. The blended powders were cold-compacted (80,000 psi) into previously degassed steel cans.
3. The steel cans containing the cold-compacts were evacuated and were heated slowly to 482°C (900°F) until outgassing ceased, at which time the can was sealed.
4. The cans were heated to 1065°C (1950°F) and then compacted in a vertical press at a pressure of 200,000 psi, which was held for five seconds. A bottom piercing ram was used to ensure more uniform compression over the entire length of the compact.

5. The steel cans were machined off the cylinders. The compacted cylinders of beryllium were machined an additional depth of 13 mils below the beryllium-steel interface to eliminate all possible iron contamination. An additional 12 mils of metal was removed in preparation of samples for corrosion testing.

Each group of alloy additions was tested in separate autoclaves. The results of corrosion testing of the hot-compacted samples in 343°C water without any additional heat treatment are shown in Table XXV.

None of the samples in the hot-compacted condition looked promising. However, the sample with the binary additions of nickel and iron showed slightly better behavior, particularly the one with the 5000 ppm additions. The 2000 ppm aluminum alloy also showed some slight indication of improved corrosion resistance.

Additional alloy samples and control samples were corrosion tested after heat treatment. The purpose of the heat treatment was to homogenize the samples by diffusion of the alloy metal into the beryllium. Samples to be heat treated were wrapped in tantalum sheet and sealed in quartz capsules under a partial pressure of argon. After the capsules were heated for a period of 24 hours at a specified temperature, they were submersed into cold water without being broken. This method of cooling was not a quench, since it was noted that the samples remained at red heat for a measurable length of time after the immersion. After heat treatment, a minimum of 2 to 3 mils was removed from all surfaces of the samples in order to eliminate traces of tantalum contamination.

The results of corrosion testing of samples heat treated at 1093°C (2000°F) for 24 hours are shown in Table XXVI. The aluminum and magnesium additions were heat treated at 982°C (1800°F).

It is evident that, in the case of the Mg, Al, Si, Cr, Mn, and Fe additions, these heat treated compacts showed no improvements as compared to the as-hot-compacted state. The control sample of CR-grade powder showed no improvement, but the control sample of QMV powder now showed good corrosion resistance. In addition, the binary 4000 ppm nickel alloy and the ternary alloys with nickel and iron additions showed good corrosion resistance after the heat treatment.

Exposure of the heat-treated samples (1093°C for 24 hours) to 343°C water was continued. The results of continued exposure are shown in Table XXVII. In addition, the corrosion results on other samples of these same materials which had been heat treated for 24 hours at 982°C and 1038°C are shown in Table XXVII.

It is evident from the data in Tables XXV, XXVI, and XXVII that heat treatment of these samples is a prerequisite for good corrosion resistance. In addition, there is some indication that the heat-treatment temperature for best corrosion resistance of the alloy containing 4000 ppm nickel was 1038°C. Corrosion of the sample heat treated at 1093°C showed the formation of white oxide spots. However, there was no indication of progressive attack on the sample.

The microstructure of five different powder alloy samples was examined for evidences of segregation. These included the alloys containing 2000 ppm Al, 2000 ppm Mn, 4000 ppm Ni, 2000 ppm Ni + 2000 ppm Fe, or 5000 ppm Ni + 5000 ppm Fe. No segregation was evident in the microstructure of any of the alloys. Figure 11, taken at a magnification of 250X, shows the alloy containing 2000 ppm Ni + 2000 ppm Fe in the as-hot-compacted and in the heat-treated conditions. These microstructures are typical of all the alloys examined. In addition, samples prepared from Pechiney CR-grade powder and from Brush QMV powder with no additions showed identical microstructures. Heat treatment resulted in only slight grain growth. X-ray examination indicated that recrystallization had occurred as a result of heat treatment at 1093°C.

Analyses of the alloys that showed promising corrosion resistance were made in order to confirm the amounts added. The results are shown in Table XXVIII. The actual analyses showed excellent agreement with the amounts added.

The results of corrosion tests have shown that it is possible to start with relatively pure beryllium (Pechiney CR-grade), which invariably corrodes rapidly, and to obtain corrosion-resistant material by the proper combination of alloying and heat treatment. Alloys containing 4000 ppm nickel, 2000 ppm iron plus 2000 ppm nickel, or 5000 ppm iron plus 5000 ppm nickel show promise of surviving extended exposure in 343°C water. Longer exposure times are necessary to demonstrate whether these alloys would be more corrosion resistant to high-temperature water corrosion than unalloyed beryllium.

Material prepared from Brush QMV-grade powder showed good corrosion resistance, whereas metal prepared from the higher purity Pechiney CR-grade powder without alloying showed very poor corrosion resistance. Thus far, the specific metallic impurity or combination of impurities responsible for the superior corrosion behavior of metal fabricated from relatively impure (Brush QMV) beryllium powder is not known. None of the alloys prepared in this program with single additions in amounts approximating their content in QMV duplicated the corrosion resistance of QMV beryllium. However, this suggests the possibility that a combination of these impurities is the key to obtaining corrosion-resistant beryllium. It is possible that small amounts of <u>multiple</u> alloy additions may produce material with corrosion behavior equal to or better than that of QMV beryllium. If the proper combination is found, it may be possible to keep the total alloy content below the 4000 ppm content of nickel or combinations of nickel plus iron studied in this program.

VI. CONCLUSIONS

It has been shown that both high-purity beryllium prepared by distillation and/or zone-refining, and commercial high-purity beryllium invariably corrode catastrophically in exposures of two days or less to 343°C water. This poor corrosion resistance was exhibited even in samples fabricated by powder metallurgical techniques.

On the positive side, it has been demonstrated that the high-purity beryllium can be made to show good corrosion resistance by alloy additions of nickel or combinations of nickel and iron (4000 ppm Ni, 2000 ppm Ni plus 2000 ppm Fe, or 5000 ppm Ni plus 5000 ppm Fe). Heat-treated samples of these alloys prepared from Pechiney CR-grade powder have indicated excellent corrosion resistance in 343°C water for as long as 43 days with still no sign of attack.

On the other hand, a control sample prepared from Pechiney CR-grade powder with no additions, processed in the same manner as the alloys, was completely converted to oxide after just three days in 343°C water. Alloy additions made individually, which showed no effect in improving the corrosion resistance of high-purity beryllium even after heat treatment, included up to 2000 ppm of Al, Mg, Mn, Si, Fe, Ni, or up to 3000 ppm Cr. Samples of beryllium prepared from Brush QMV powder with no additions also have shown good corrosion resistance after heat treatment.

Unalloyed beryllium metal fabricated by powder metallurgy from less pure commercial powders (e.g. Brush QMV grade) is capable of good corrosion resistance in 343°C water for at least up to about 160 days. However, samples of the materials which survived 160 days in test also showed failure in shorter times. Data were obtained which showed that copper contamination in the water caused accelerated corrosion of beryllium samples in an unpredictable manner. Copper was present on the samples that showed a sudden breakdown in corrosion resistance after long exposure. There is good reason to believe now that beryllium prepared directly from commercial powders is capable of surviving for extended periods of time well beyond 160 days, in 343°C water which is copper-free.

Heat treatment appears to have a significant effect on corrosion behavior. Alloy additions to Pechiney CR-grade powder of 4000 ppm Ni, 2000 ppm Ni plus 2000 ppm Fe, or 5000 ppm Ni plus 5000 ppm Fe all showed poor corrosion resistance when tested as hot compacted, as did a sample of beryllium prepared in the same manner from Brush QMV powder with no additions. When these materials were heat treated for 24 hours at 982, 1038, or 1093°C, a definite improvement in corrosion resistance was noted in every instance.

Studies on the effects of aging heat treatments were made before it was discovered that other effects of test conditions caused erratic corrosion. The results obtained were very erratic, so definite conclusions could not be drawn from the data.

Surface preparation was found to influence corrosion behavior. Removal of surface metal by etching samples of hot-pressed or extruded beryllium powder invariably caused the sample to show poor corrosion behavior in high-temperature water. In addition, it was found that removal of 12 to 14 mils from the surface of the corrosion samples by polishing appeared to render the sample less susceptible to attack than if lesser amounts were removed.

Experiments indicated that boiling on the surface of water corrosion samples at high temperature causes accelerated corrosion. This local boiling on the beryllium samples might have been responsible in part of the erratic corrosion behavior encountered in this investigation. An overpressure of argon in the autoclaves was used to eliminate local boiling as a cause of corrosion resistance breakdown.

Tests were made to determine whether the corrosion behavior of beryllium could be influenced by the starting pH of the water, which was varied by adding small amounts of different chemicals to water. Some of the results were conflicting (probably for other reasons), but in general it appeared that the pH by itself has no major effect on the corrosion in the range of 6 to 8. There was some suspicion that the effect of copper contamination on corrosion behavior is interrelated with pH. It was frequently observed that, when a low pH was recorded after a test, heavier than normal amounts of copper were noted on samples, and samples in general showed accelerated local attack. Most of the corrosion test runs gave pH values from 6.2 to 7.5. However, pH values as low as 5.1 and as high as 10.5 were recorded. There has been no explanation for these variations in pH, except in the case of the 10.5 value, where numerous samples in test had completely disintegrated.

Samples of beryllium which were exposed to 343°C water in contact with platinum, zirconium and Zircaloy-2 showed no evidence of galvanic corrosion. Beryllium samples clamped between non-oxidized stainless-steel blocks showed attack, in some instances, of only the surface contacting the stainless steel. It is not known whether the attack was galvanic or possibly due to crevice corrosion. There was no evidence in this investigation to indicate that there was galvanic corrosion between beryllium and the support trays of oxidized stainless-steel screening.

The results of corrosion testing different types of beryllium in 400°C steam at 1500 psi were similar in many respects to corrosion behavior of the samples of the respective materials in 343°C water. Samples showing good corrosion in 343°C water also showed relatively good corrosion in 400°C steam. Samples which corroded badly in 343°C water also showed poor corrosion resitance in steam. The localized attack in steam was somewhat more severe and appeared to progress with increased exposure time, whereas in water corrosion little, if any, progression of attack was noted. Breakdown of corrosion resistance in steam occurred after 60 to 100 days, in the form of small broken oxide blisters. The corrosion resistance of different beryllium samples in 400°C steam does not look promising. No alloys were tested.

VII. SUGGESTIONS FOR FUTURE WORK

In order to clearly establish the feasibility of the use of beryllium in water-cooled reactors, it appears worthwhile to continue these investigations along the following lines.

A. Testing of Commercial-Purity Beryllium (QMV or Equivalent Berylco Grade) in High-Temperature Copper-Free Water

Beryllium appears to be capable of resisting the corrosive attack of 343°C copper-free water for some indefinite period in excess of 160 days. Additional work is necessary to establish the reliability of the metal for use in reactors by prolonged corrosion testing of a sufficient number of various types of samples to be statistically significent.

B. Copper Contamination

Relatively minute amounts of copper contamination in the water were found to be the main cause of the breakdown in the corrosion resistance of beryllium, which occurred at unpredictable times. A knowledge of the level of copper contamination that can be tolerated without affecting the corrosion resistance is necessary for control purposes. The unpredicatable corrosion breakdown of beryllium in copper-contaminated high-temperature water indicates that some other condition, possibly pH, acts to trigger the corrosion reaction. A study of this would enable the development of means of neutralizing the deleterious effect of copper contamination, to safeguard against the danger of accidental copper contamination in any practical application .

C. Alloy Studies

The present investigation indicated that individual alloy additions to high-purity beryllium up to and exceeding the amounts that these alloys are present in commercial-purity (QMV) beryllium had no effect in improving the corrosion resistance. In future work, relatively small amounts of <u>multiple</u> alloy additions would be made to high-purity beryllium in attempts to duplicate the combination of impurities in QMV beryllium presumed to be responsible for the good corrosion behavior of the material. At the same time, the elements and amounts which are detrimental to the corrosion behavior of beryllium would be determined.

As another approach, small additions of the individual elements normally present in QMV beryllium would be added to QMV beryllium for the purpose of determining whether a particular element is beneficial, detrimental or without effect on the corrosion behavior. This would also serve the purpose of specifying the tolerance limits for specific impurities in QMV beryllium.

D. Heat Treatment

The present work has shown that heat treatment has a significant effect on corrosion behavior. Further investigation to determine the limits of heat treatment of beryllium for good corrosion behavior is desirable. Variables such as time at temperature, methods of cooling, and aging effects would be studied.

E. Steam Corrosion

The corrosion resistance of unalloyed beryllium in 400°C (1500 psi) steam did not appear to be promising. It is conceivable, however, that the alloy additions of nickel and iron which showed improved corrosion resistance in high-temperature water might also show improved corrosion resistance in high-temperature steam.

VIII. REFERENCES

1. D. S. Kneppel, Corrosion of Beryllium in 600°F Water, USAEC Report NMI-1190, Nuclear Metals, Inc., Cambridge, Massachusetts, 1957.

2. S. H. Gelles (coord.), Report to Aeronautical Systems Division, Beryllium Research and Development Program, NMI-9516, Vol. I, Section 6, Nuclear Metals, Inc., Concord, Massachusetts, May 1962.

3. R. S. Peoples and J. H. Bulkowski, Corrosion of Beryllium in 525°F and 600°F Distilled Water, BMI-HAP-101, Battelle Memorial Institute, Columbus, Ohio, September 1949.

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5. H. M. Lindsay, V. D. Scott and A. Moore, Selective Decoration of Fine Structural Effects in Beryllium, J. Less Common Metals, 3 (1961) 407-411.

6. F. M. Yans, Nuclear Metals, Inc., Concord, Massachusetts, (private communication), January 1960.

7. J. E. Draley and W. E. Ruther, Aqueous Corrosion of Aluminum, Part 2: Methods of Protection Above 200°C, Corrosion 12 (1956) 20-30.

IX. BIBLIOGRAPHY OF REPORTS ISSUED

The following reports were issued during the course of this contract:

NMI-1901, Progress Report for May 1962

NMI-1902, Progress Report for June 1962

NMI-1903, Quarterly Progress Report from April 1962 through July 1962.

NMI-1904, Progress Report for August 1962

NMI-1905, Quarterly Progress Report from July 1962 through September 1962.

NMI-1906, Progress Report for October 1962

NMI-1907, Progress Report for November 1962

NMI-1908, Quarterly Progress Report from September 1962 through December 1962

NMI-1909, Progress Report for January 1963

NMI-1910, Progress Report for February 1963

TABLE I

Vendors' Analyses of Beryllium

	Extruded Brush QMV Powder	Hot Pressed Brush QMV Powder	Vacuum Melted and Extruded CR Grade Pechiney Flake
Assay Be	99.0 $^w/_o$	99.2 $^w/_o$	--
BeO	1.01	0.8	<0.4 $^w/_o$
Fe	0.073	0.114	<0.014
Al	0.060	0.080	<0.005
Ni	0.013	--	0.0095
Si	0.030	0.025	0.0020
C	0.10	0.11	0.018
Mg	0.020	0.005	0.001

TABLE II

Effect of Surface Preparation on Corrosion Resistance in 343°C Water

Material	Sample No.	Surface Preparation(1)	Weight Gain, mg/dm^2							
			Exposure Time, days							
			1	3	5	9	16	23	37	51
Extruded Brush QMV Powder	36-1	W/320 - 1 mil	18	-	48					
	36-2	W/320 - 1 mil	18	-	210					
	19-2	W/320 - 12 mils, H/0000	-	180	134	-88N(2)				
	19-5	S/240 - 12-14 mils	-	33	-	22	33	30	35	48
	19-6	S/240 - 12-14 mils	-	30	-	25	35	35	35	
	19-9	S/240 - 10-12 mils, W/320 - 3 mils	-	20	-	18	27	27	27	35
	19-10	S/240 - 10-12 mils, W/320 - 3 mils	-	23	-	13	15	23	23	23
Hot-pressed QMV powder	36-3	W/320 - 2 mils	30	-	905N					
	36-4	W/320 - 2 mils	13	-	558N					
	19-1	W/320 - 10-11 mils, H/0000	-	36	-	54	-252N			
	19-3	S/240 - 12-14 mils	-	64	-	44	56	60	60	60
	19-4	S/240 - 12-14 mils	-	57	-	40	51	57	57	53
	19-7	S/240 - 10-12 mils, W/320 - 3 mils, W/400	-	40	-	27	39	39	39	39
	19-8	S/240 - 10-12 mils, W/320 - 3 mils, W/400	-	53	-	49	46	-37	119N	
Vacuum melted and extruded, CR grade Pechiney Flake	19-25	W/320 - 13 mils, H/0000	Heated to 343°C and cooled. Heavy cracked oxide covered most of sample.							

(1) W - polishing wheel, S - belt sander, H - hand. All polishing done wet. S/240 - 10-12 mils, W/320 - 3 mils, W/400 indicates removal of 10-12 mils per surface on belt sander using 240 grit paper, followed by polishing wheel removing 3 mils with 320 grit and finishing with 400 grit with a negligible amount of metal removed.

(2) N - non-adherent oxide.

TABLE III

Corrosion of Beryllium in 400°C Steam at 1500 psi

	Sample No.	Time (days)	Appearance
Hot-pressed Brush QMV powder (Table I)	35-1	62	Pitted; oxide spots; metal lifting up.
	35-2	62	" " " " " "
Extruded Brush QMV powder (Table IV, Batch 444)	35-4	62	Pitted; oxide spot; metal lifting up.
	35-3*	90	Numerous deep pits; oxide spots.
Extruded Brush QMV powder (Table I)	35-5	103	Numerous broken oxide blisters.
	35-6	76	Broken oxide blisters.
Extruded Brush QMV -325 mesh powder (Table IV, Batch 437)	35-7	103	Broken oxide blisters.
	35-8	103	" " "
Vacuum-melted and extruded CR Grade Pechiney Flake (Table I)	35-9	1	Heavy oxide.

* Sample aged at 500°C for 1 week.

TABLE IV

Analysis ($^{w}/_{o}$) of Brush QMV Powder (-200 Mesh)

	Batch 437 (for -325 mesh, Batch 444 see note)	
BeO	0.79	--
Fe	.062	.11
Al	.018	--
Ni	.012	.014
Si	.067	.060
C	--	--
Mg	.020	.070
Cu	--	.003
Mn	.007	.006
Cr	.007	.007

Note: Analysis of sieved -325 mesh powder was essentially the same as that for Batch 437 (-200 mesh) except for higher BeO content, 1.14 $^{w}/o$ as compared to 0.79$^{w}/o$.

TABLE V

Corrosion of Beryllium in 650°C Steam at Atmospheric Pressure

Material	Time (hrs)	Observations
Brush QMV powder, hot pressed	2	Tiny broken blisters on all surfaces.
Brush QMV powder, extruded	2	Tiny broken blisters on all surfaces.
Pechiney -200 CR powder, hot pressed	2	Tiny broken blisters on all surfaces.
NMI distilled	2	No attack except for crack.
Pechiney SR Flake, extruded, NMI zone refined, 5 passes	26	Cracks; one area metal raised; some areas of small blisters.
Pechiney SR Flake, extruded	2	Numerous round oxide spots on transverse faces. Oxide non-adherent in many spots.
Pechiney SR powder -110 mesh, sintered and extruded	2	A few broken small blisters on transverse face. Blister striations parallel to extrusion direction on circumference.
Pechiney SR grade, cast and extruded	500	No evidence of attack.
Pechiney CR powder -110 mesh, sintered and extruded	2	Blister striations parallel to extrusion direction. Transverse face roughened.
Pechiney CR grade, cast and extruded	26	Blisters on circumference.
NMI zone refined, 5 passes	26	Grey film, metal spalling in some areas. Some areas blistered.

TABLE VI

Effect of Aging on the Corrosion of Extruded QMV Beryllium in Water at 343°C

Heat Treatment, Coupons A and B	Appearance After 3 Days
As-extruded	Uniform attack, thick oxide
Solutionized (1100°C for 1 hr and then water quenched)	Complete disintegration
Solutionized as above, aged 2 hrs at 500°C and water quenched	Shallow pits, one area of heavy oxide
Solutionized as above, aged 24 hrs at 700°C and water quenched	Uniform attack, thick oxide

TABLE VII

Effect of Aging on the Corrosion of Extruded QMV -325 Mesh Beryllium in Water at 343°C

Heat Treatment*	Time (days)	Appearance
Aged 500°C - 2 hrs	23 23	Raised areas of oxide " " "
Aged 550°C - 96 hrs**	4 4	Raised areas of oxide " " "
Aged 700°C - 24 hrs	23 23	Raised oxide in edges, flaking Partial disintegration
Solutionized 1100°C - 1 hr	23 23	Disintegrated "
Solutionized 1100°C - 1 hr Aged 500°C - 2 hrs	23 23	Heavy white oxide " " "
Solutionized 1100°C - 1 hr Aged 700°C - 24 hrs	23 9	Heavy white oxide " " "
As-extruded**	169	A few spots of raised oxide

* Samples quenched into water after aging or solutionizing.

** These samples were not tested as part of this series.

TABLE VIII

Vendor's Analysis of Pechiney Samples

	Sample No.					
	1 Extruded SR Flake	2 Ext. Cast CR Flake	3 Ext. Sintered CR -110 mesh	4 Ext. Sintered SR -110 mesh	5 Ext. Cast SR Flake	6 Hot Pressed -200 mesh CR
BeO	3100 ppm	0.5%	1.2%	0.9%	0.2%	1.41%
Cl	605 "	50 ppm	50 ppm	10 ppm	10 ppm	
Fe	200 "	400 "	300 "	56 "	56 "	270
Si	<50 "	70 "	<50 "	<20 "	<20 "	55
Cu	<10 "	20 "	30 "	13 "	13 "	
Mn	10 "	30 "	10 "	18 "	18 "	
Mg	<10 "	20 "	<10 "	<10 "	<10 "	10
Ti	ND "					
Al	<50 "	150 "	150 "	<30 "	<30 "	
Ni	30 "	120 "	120 "	61 "	61 "	
Cr	10 "	ND "	ND "	6 "	6 "	
C	450 "	190 "	190 "	165 "	165 "	150
Zn	<50 "					
Na	<80 "					
B	< 2 "					

Note: The temperature of all extrusions was in the range of 950-980°C and the reduction ratio about 31:1, except sample 1 where the reduction ratio was 100:1. The extruded rods were air cooled and then subsequently heat treated at 850°C.

TABLE IX

Typical Analyses of Various Beryllium Types

Type	Analyses in ppm						
	BeO	C	Fe	Ni	Al	Si	Mg
Brush QMV powder -200 mesh	10,000	1,000	1500	100	600	300	100
Pechiney CR flake	12,000	190	300	120	150	<50	<10
Pechiney SR flake	9,000	165	60	60	30	<20	<10
NMI Distilled	~150	-	2-3	1-2	15	<20	
NMI Zone refined - 5 pass Vacuum melted CR Flake Start end			49	215	19		
NMI Zone refined - 6 pass Vacuum melted SR flake Start end			5	80	<5	15	
NMI Zone refined - 6 pass Distilled Freeze end			13	1	18	<20	

TABLE X

Vendor's Analyses of Beryllium Compacts

(ppm)

	Brush Compact No.				Beryllium Corp. Compact No.				
	1	2	3	4	5	6	7	8	9
BeO (%)	.77	2.	.87	4.7	1.5-2	2.5	1	4-5	2-3
Fe	500	1500	1200	1700	1500-1700	1800	1450	2200	1300-1400
Al	200	700	800	800	500-800	400	850	1000	300
Mg	<100	<100	<100	<100	50-300	200	400	400	50-200
Si	<200	600	400	600	400-700	400	300	650	400
C	1000	1200	1500	1700	1100-1300	1500	1000	3000	2200
Cd	< 0.7								
Ca	100								
Cr	100								
Co	2								
Cu	130								
Pb	10								
Li	1								
Mn	<100								
Mo	< 20								
Ni	100								
N	140								
Ag	3								

TABLE XI

Corrosion Testing in 343°C Water

Brush Beryllium and Berylco Extruded Compacts

Run	Compact No.	Coupon	Exposure Time (days)		Appearance
			Before Failure	At Failure	
44	1	A	4	8	Raised cracked oxide on edges
		B	4	8	" " " " "
	2	A	4	8	Cracked oxide spots edges and center
		B	4	8	" " " " " "
	3	A	4	8	Heavy cracked oxide spots
		B	4	8	" " " "
	4	A	4	8	Disintegrated
		B	4	8	"
	5	A	4	8	Oxide spot on edge
		B	4	8	" " " "
	6	A	14	21	Deeply pitted
		B	14	21	" "
	7	A	14	21	" "
		B	14	21	" "
	8	A	14	21	" "
		B	14	21	" "
	9	A	14	21	" "
		B	14	21	" "
64	1	A	35		Localized pitting
		B	68		" "
	2	A	1	4	Raised oxide on edges
		B	1	4	" " " "
	3	A	1	4	" " " "
		B	7	14	Raised oxide spots
	4	A	1	4	Disintegrated
		B	-	1	Heavy general oxide
	5	A	1	4	Raised oxide on edge
		B	68		Localized pitting
	6	A	7	14	Oxide spot
		B	1	4	Oxide spot on edge
	7	A	68		Localized pitting
		B	71		" "
	8	A	68		" "
		B	71		" "
	9	A	68		" "
		B	71		" "

TABLE XII

Typical Analysis of NMI Distilled Beryllium

Impurity	Conc. (ppm)
Fe	3
Ni	2
Cr	1
Mn	5
Si	12
Al	20
Cu	5
Ta	<2
N	5
Sc	<0.1
O	$\sim$100

TABLE XIII

Zone-Refined Stock

Sample No.	History
1	Vacuum melted Pechiney Flake; 3 passes
2	Vacuum melted Pechiney Flake; 5 passes
3	Distilled beryllium; 3 passes
4	Double distilled; 6 passes

TABLE XIV

Powder Extrusions

Source	Particle Size
Pechiney SR grade powder	-110 mesh
Brush QMV grade powder	-200 mesh
NMI double distilled	coarse unsized powder estimated 1-500 μ, average 100 μ
Vacuum-melted Pechiney CR flake	coarse unsized powder estimated 1-500 μ, average 100 μ

TABLE XV

Effect of Boric Acid Addition on Corrosion of Hot-Pressed QMV Beryllium in 343°C Water

Additive to Water	Conc. (ppm)	Initial pH	Final pH	Corrosion Resistance Good (days)	Corrosion Resistance Failed (days)	Remarks
None	---	---	6.1-7.5	34	42	Blister oxide. pH at failure, 5.8.
None	---	---	6.4-7.1	26	34	Blister oxide. pH at failure, 5.8.
Boric Acid	500	6.2	6.2-6.5	21	35	One sample started to fail at 21 days. Heavy white oxide, 35 days. pH, 6.4.
Boric Acid	500	6.2	6.2-6.4	7	23	Some indication of attack after 9 days. Heavy attack, 23 days. pH, 6.4.

TABLE XVI

Effect of pH on Corrosion of Hot-pressed QMV Beryllium in 343°C Water

Additive to Water	Concentration of PO_4 (ppm)	Initial pH	Exposure Time (days)	Final pH	Appearance of Samples
Na_2HPO_4	80	8.5	5	7.6	Heavy general oxide.
Na_2HPO_4 + NaH_2PO_4	40 + 40	7.0	5	10.6	Heavy general oxide.
NaH_2PO_4	20	5.5	6	6.2*	Good

* A three-day run in an auto-clave with no samples showed a final pH of the water of 6.3.

TABLE XVII

Effect of Copper Contamination on the Corrosion Behavior in 343°C Water of Brush QMV Beryllium

Material	Run No.	pH	Cumulative Time-days	Coupon	Appearance
Hot-pressed -200 mesh powder	1	6.2	7	A	Heavy oxide one surface; discontinued.
	1	6.2	7	B	Numerous small white oxide spots, all surfaces.
	2	8.6	14	A	White oxide layer flaking; discontinued.
Extruded -200 mesh powder*	1	6.2	7	A	White oxide spots on all surfaces, very numerous on one surface.
	1	6.2	7	B	White oxide spots on all surfaces.
	2	8.6	14	A	Numerous white oxide spots.
	2	8.6	14	B	Disintegrated
	3	6.7	21	A	No significant change from 14-day exposure.
Extruded -325 mesh powder**	1	6.2	7	A and B	Numerous white oxide spots on all surfaces.
	2	8.6	14	A and B	No change from 7-day exposure.
	3	6.7	21	A and B	No change from 14-day exposure.

* See Table XVIII, sample 11-1 for long-term corrosion data.

** See Table XVIII, sample 26-2 and 27-2 for long-term corrosion data.

TABLE XVIII

Corrosion of Beryllium in 343°C Water

Sample	Material	Good Corrosion Resistance, Time (days)	Failure Time (days)	Appearance
11-1	Brush QMV (-200 mesh) extruded	162	169	Thick cracked oxide on edges.
11-4	Brush QMV (-200 mesh) extruded	154	161	Thick cracked oxide on edges
11-5*		162	169	Spots of raised oxide.
26-2	Brush QMV (-325 mesh) extruded	111	118	White oxide spots.
27-2	Same powder batch as 11-1.	102	109	White oxide spots.

* Sample heat treated at 560°C for one week prior to corrosion test.

NOTE: All samples were in test in same autoclave at time of failure. The pH of the water at time of failure was 6.4.

TABLE XIX

Effect of Distilled Beryllium Addition* on Corrosion of Hot-pressed QMV Beryllium in 343°C Water

Exposure Time (days)	Cumulative Time (days)	pH of Water at End of Each Test Run	Appearance of Samples
5	--	7.6	Good
7	12	6.9	Good
7	19	7.1**	Good
7	--	5.9	Good
7	14	7.1**	Good

* Solid pieces of distilled beryllium present in autoclave during test.

** Both sets of samples combined for testing in same autoclave.

TABLE XX

Effect of Metallic Additives on Corrosion of Hot-Pressed QMV Beryllium in 343°C Water

Addition to Water	Time (days)	pH	Appearance
NiO	3	6.6	Good
	7	6.4	Surface rough, one corner spalled oxide
CuO	3	6.5	Copper precipitate, good
	7	6.7	Copper precipitate, good
	13	6.7	Copper precipitate, roughened spots on samples
Fe	3	6.8	Some localized attack
	7	6.2	Heavy oxide spots on some surfaces
Cr	3	6.0	Good
	7	6.2	Normal local attack
Al	3	7.1	Good
	7	6.4	Normal local attack
Mn	5	6.3	Heavier than normal local attack
	8	6.4	May be some raised oxide
Mg	5	6.5	Good

TABLE XXI

Vendor's Analysis of Pechiney SR-Grade Flake Beryllium

(Starting metal for extruded cast alloys)

Element	ppm
Cr	< 2
Ca	<30
Ni	30
Zn	30
Cu	10
Al	<30
Si	18
Ti	< 2
Mg	<10
Mn	10
B	1
Na	150
BeO	.06%
Cl	600
C	110

TABLE XXII

Analyses of Extruded Cast Beryllium Alloys - Nominal 1 $^w/_o$

Element	$^w/_o$		
	Front	Middle	Rear
Co	0.69	0.69	0.69
Ni	1.34	1.00	0.55
Cr	0.79	0.79	0.79
Al	--	--	--

TABLE XXIII

Vendors' Analyses of -200 Mesh Beryllium Powder

Element	Pechiney CR-Grade (ppm)	Brush QMV-Grade (ppm)
Al	220	700
Ag	<3	
B	1	
Cd	<2	
Ca	<30	
C	150	1000
Cr	<10	
Cu	16	
Fe	205	1200
Cl	<20	
Mg	<10	100
Mn	5	
Mo	<15	
Ni	235	
Pb	<15	
Si	255	300
Na	<100	
Zn	<80	
F	<100	
Li	0.89%	1.06%

TABLE XXIV

Alloy Additions to Pechiney CR-Grade Beryllium Powder (-200 Mesh)

Addition Element	Amounts (ppm)	Powder Size of Addition
Control	No addition, CR powder	-200 mesh Be
Al	400, 1000, 2000	-325 mesh
Cr	500, 1000, 3000	-200 mesh
Mg	200, 500, 2000	40 mesh
Mn	200, 500, 2000	-200 mesh
Ni	800, 2000, 4000	Mond carbonyl powder 7-9 microns
Si*	300, 1000, 2000	-200 mesh
Fe	600, 1000, 2000	-200 mesh
Ni + Fe	2000 + 2000 5000 + 5000	

* Silicon powder of somewhat coarser mesh was used in the 300 and 1000 ppm additions.

NOTE: A comparison sample of -200 mesh QMV powder with no additions was also prepared.

TABLE XXV

Corrosion of Hot-Compacted CR-Grade Beryllium Alloys in 343°C Water

Alloy	Amounts (ppm)	Time (days)	pH	Appearance
Control	(CR powder)	3	6.9	Disintegrated
Mg	200, 500, 2000	3	7.1	Disintegrated
Al	400, 1000	1	7.0	Disintegrated
	2000	3*	6.9	Disintegrated
Si	500, 1000, 2000	3	6.9	Disintegrated
Cr	500, 1000, 3000	3	6.9	Disintegrated
Mn	200, 500, 2000	2	6.9	Disintegrated
Fe	600, 1000, 2000	3	7.1	Disintegrated
Ni	800, 2000, 4000	4	6.8	2000 ppm showed very heavy oxide, others disintegrated.
Ni + Fe	2000 + 2000	3	8.0	Partial disintegration
Ni + Fe	5000 + 5000			Heavy oxide, some metal still visible.

Comparison sample prepared from Brush QMV powder (no additions).	3	6.9	Disintegrated

* After one-day exposure, sample looked good except one spot of white oxide.

TABLE XXVI

Corrosion of Hot-Compacted CR-Grade Beryllium Alloys in 343°C Water

(Heat treated at 1093°C for 24 hours*)

Alloy	Amounts (ppm)	Time (days)	pH	Appearance
Control	CR Powder	3	5.9	Disintegrated
Mg	200, 500, 2000	3	7.0	Disintegrated
Al	400, 1000, 2000	2	7.0	Disintegrated
Si	300, 1000, 2000	2	6.9	Disintegrated
Cr	500, 1000, 3000	3	6.9	Disintegrated
Mn	200, 500, 2000	2	6.9	Disintegrated
Fe	600, 1000, 2000	3	7.1	Disintegrated
Ni	800, 2000	4	6.8	Disintegrated
Ni	4000	4	6.8	Good except for white oxide in isolated grains
Ni + Fe	2000 + 2000, 5000 + 5000	6	7.4	Good, no attack

Comparison sample prepared from Brush QMV powder (no additions). Heat treated at 1093°C for 24 hours.	3	5.9	Good, no attack

* Mg and Al alloy additions were heat treated at 982°C (1800°F) for 24 hours.

TABLE XXVII

Corrosion of Hot-Compacted CR-Grade Alloys in 343°C Water

Alloy Addition to Pechiney CR Powder	Amount (ppm)	24-Hour Heat Treatment (°C)	Exposure Time (days)	Appearance
Ni	4000	As-compacted	4	Disintegrated
		982	3	Heavy grey oxide
		1038	4	Good
		1093	58	Oxide in isolated grains
Ni + Fe	2000 + 2000	As-compacted	3	Partially disintegrated
		982	21	Good
		1038	11	Good
		1093	57	Good
Ni + Fe	5000 + 5000	As-compacted	3	Heavy white oxide structure
		982	21	Good
		1038	11	Good
		1093	57	Good

Comparison sample prepared from Brush QMV Powder (no additions)	As-compacted	3	Disintegrated
	982 (1800°F)	21	Good
	1038 (1900°F)	11	Good
	1093 (2000°F)	15	Raised oxide on some surfaces*

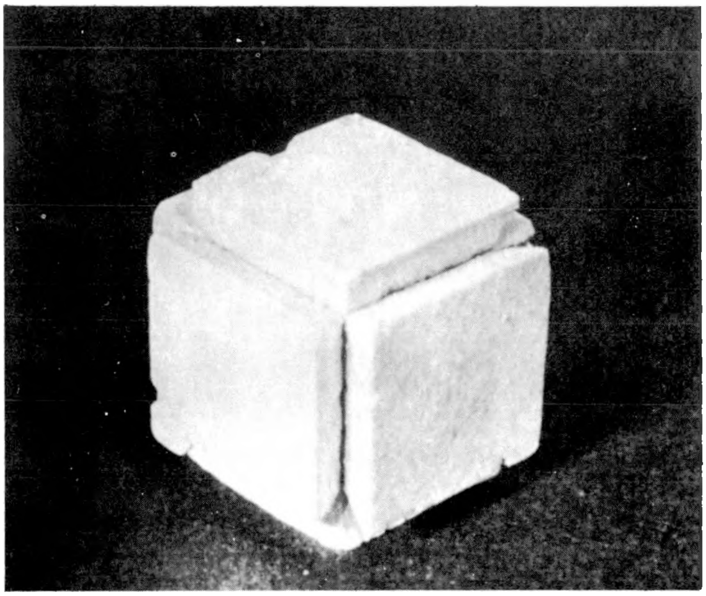
* Sample was in autoclave by itself where considerable copper deposition on sample was noted and the pH of the water was 5.8. This may have been the cause of premature failure of the sample.

TABLE XXVIII

Chemical Analyses of Hot-Compacted Beryllium Alloys

Alloy	Amount Added (ppm)	Amount Present* in Be (ppm)	Actual Analysis (ppm)
Ni	4000	235	4100
Ni + Fe	2000 + 2000	235 + 205	1970 + 2270
Ni + Fe	5000 + 5000	235 + 205	4940 + 4830

* Vendor's analyses of Pechiney CR-grade powder to which alloying additions were made.



2.5X RF-9070

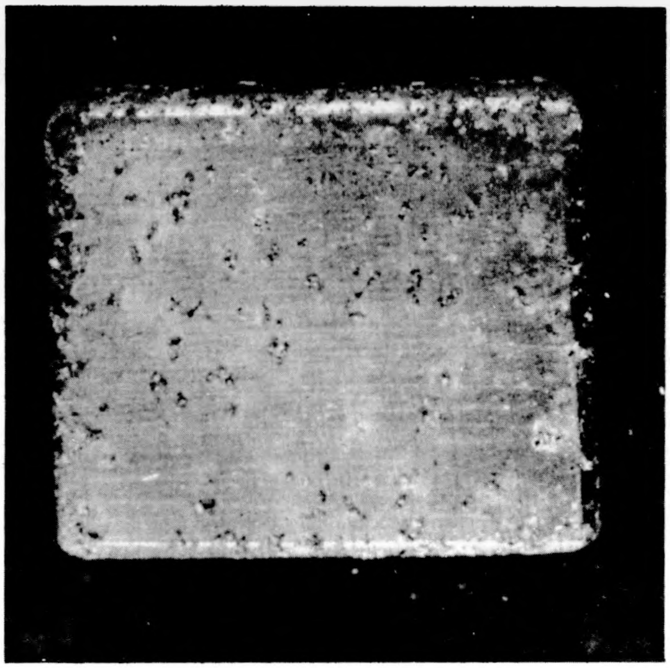
Fig. 1 - General corrosion attack. Sample appears to have been completely converted to oxide.

12X RF-8827

Fig. 2 - Extruded QMV powder corroded in 343°C water for 94 days, showing arrested localized attack.

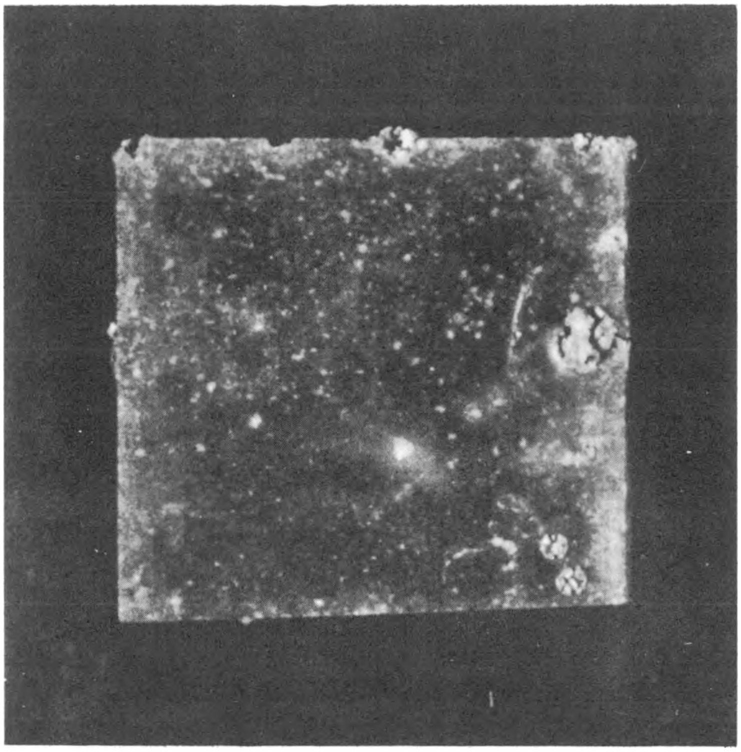
6X

Fig. 3 - Hot-pressed beryllium sample corroded in 343°C water for 122 days, showing localized pitting.



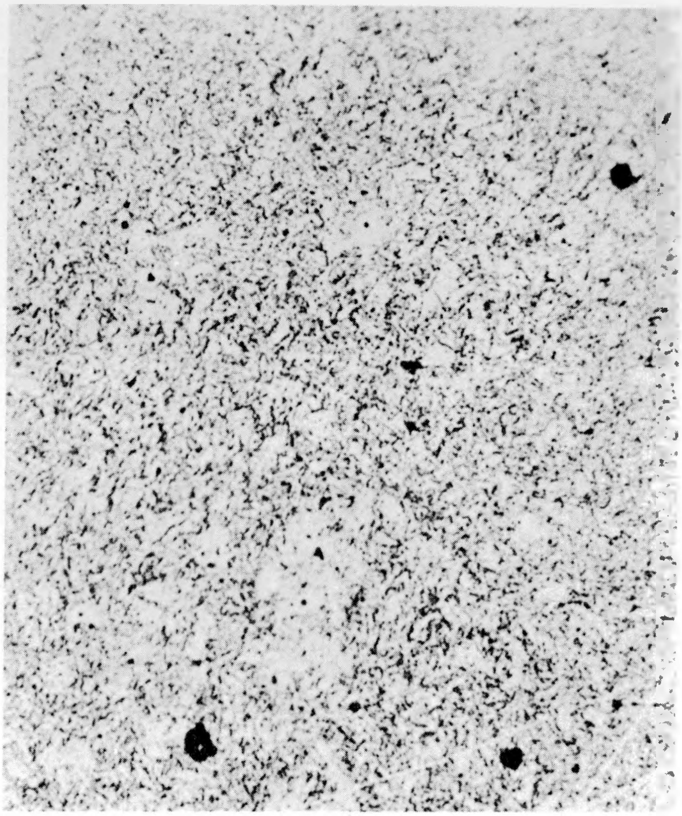
6X RF-9071

Fig. 4 - Blister-type corrosion resulting from localized boiling on surface of hot-pressed beryllium sample.



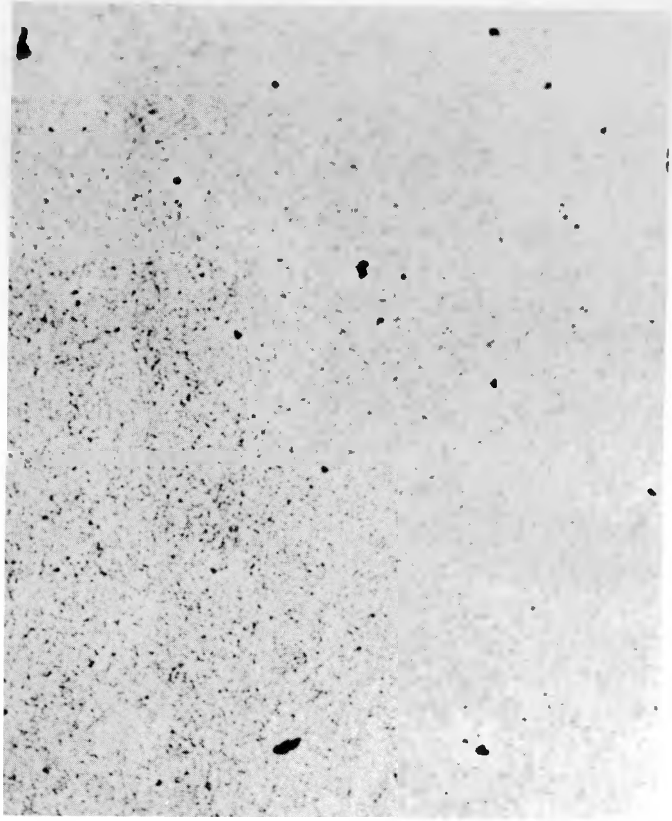
6X RF-9071 (R)

Fig. 5 - Hot-pressed beryllium sample tested in 400°C (1500 psi) steam for 62 days, showing corrosion attack.



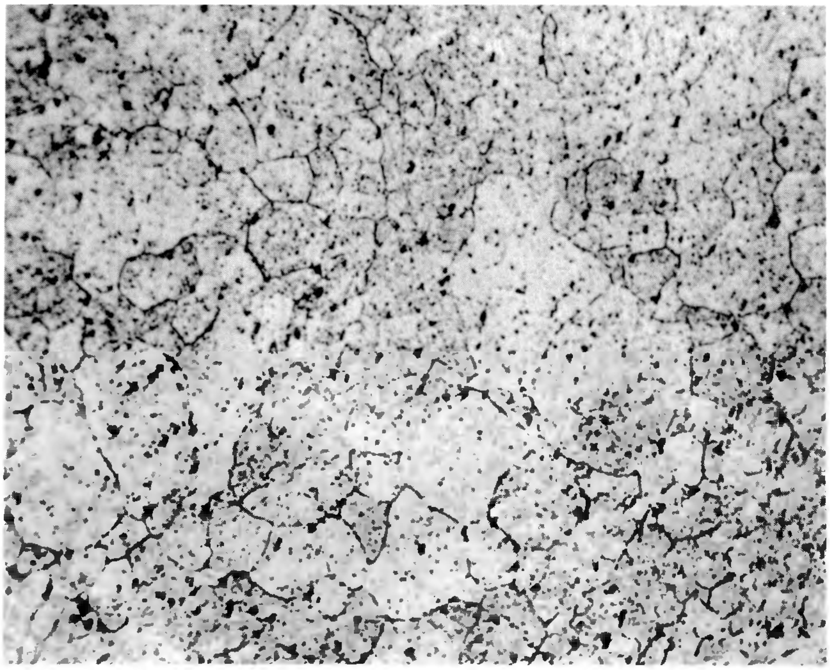
250X Bt. Lt. B 486-7

Fig. 6 - Microstructure of extruded Brush Compact No. 4. Sample showed poor corrosion resistance.



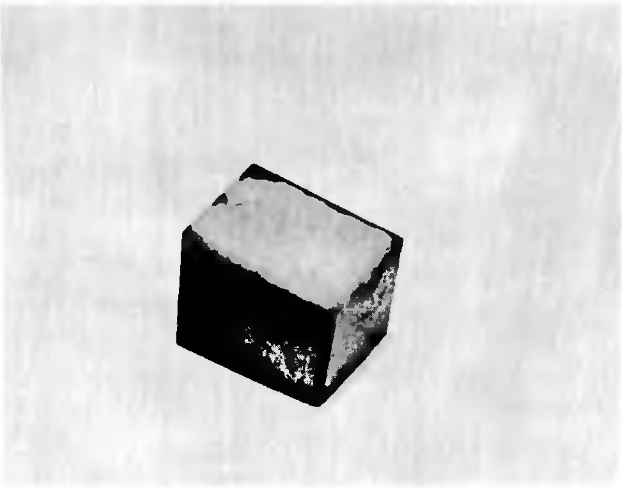
250X Bt. Lt. B 486-4

Fig. 7 - Microstructure of extruded Berylco Compact No. 7. Typical of all extruded Brush and Berylco Compacts except No. 4. Samples generally showed good corrosion resistance.



250X B 468-18

Fig. 8 - Microstructure of hot-pressed Brush QMV beryllium. Sample showed good corrosion resistance.



3X RF-9072

Fig. 9 - Hot-pressed QMV beryllium showing corroded top surface as a result of localized boiling on the surface.

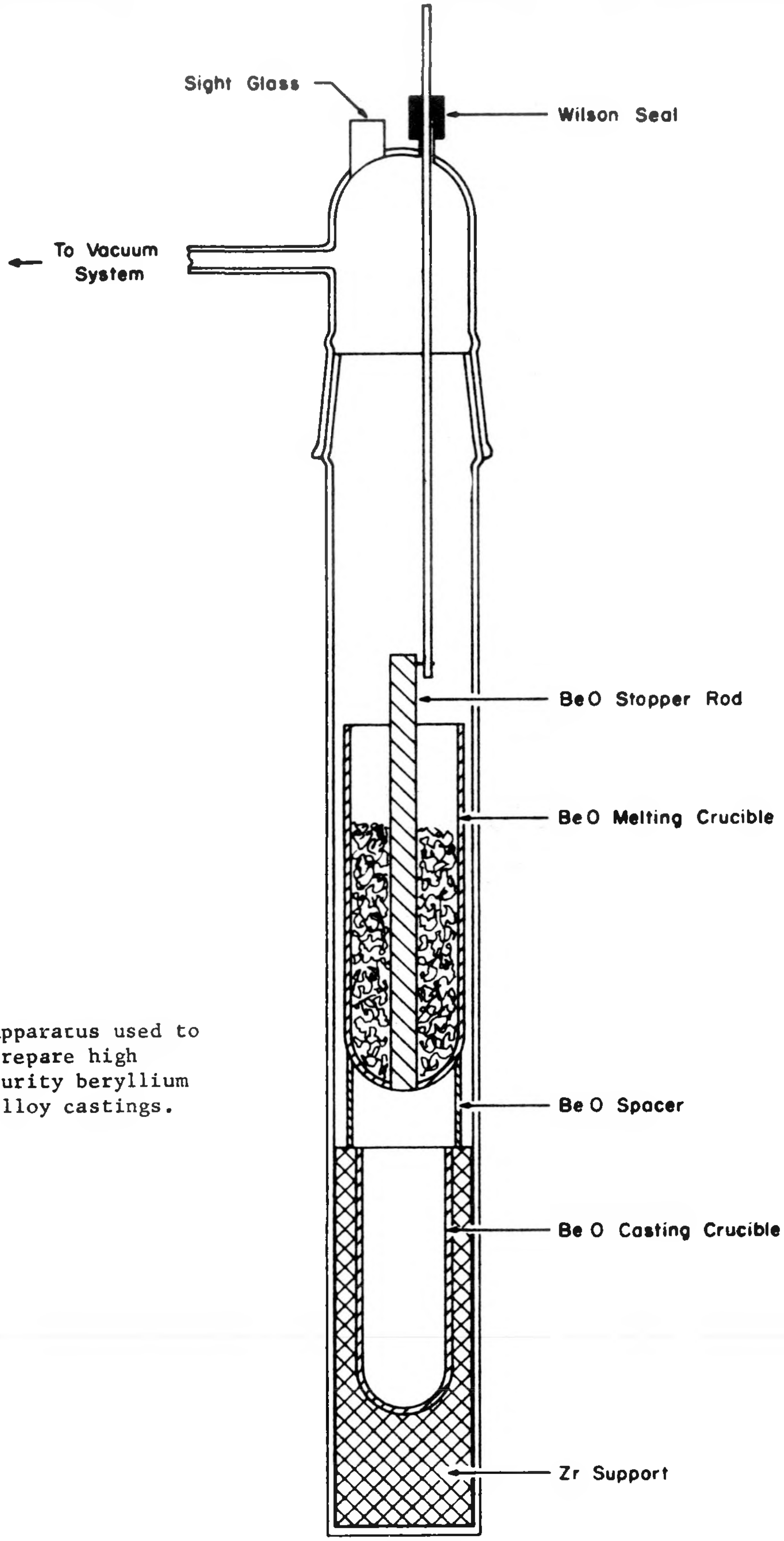
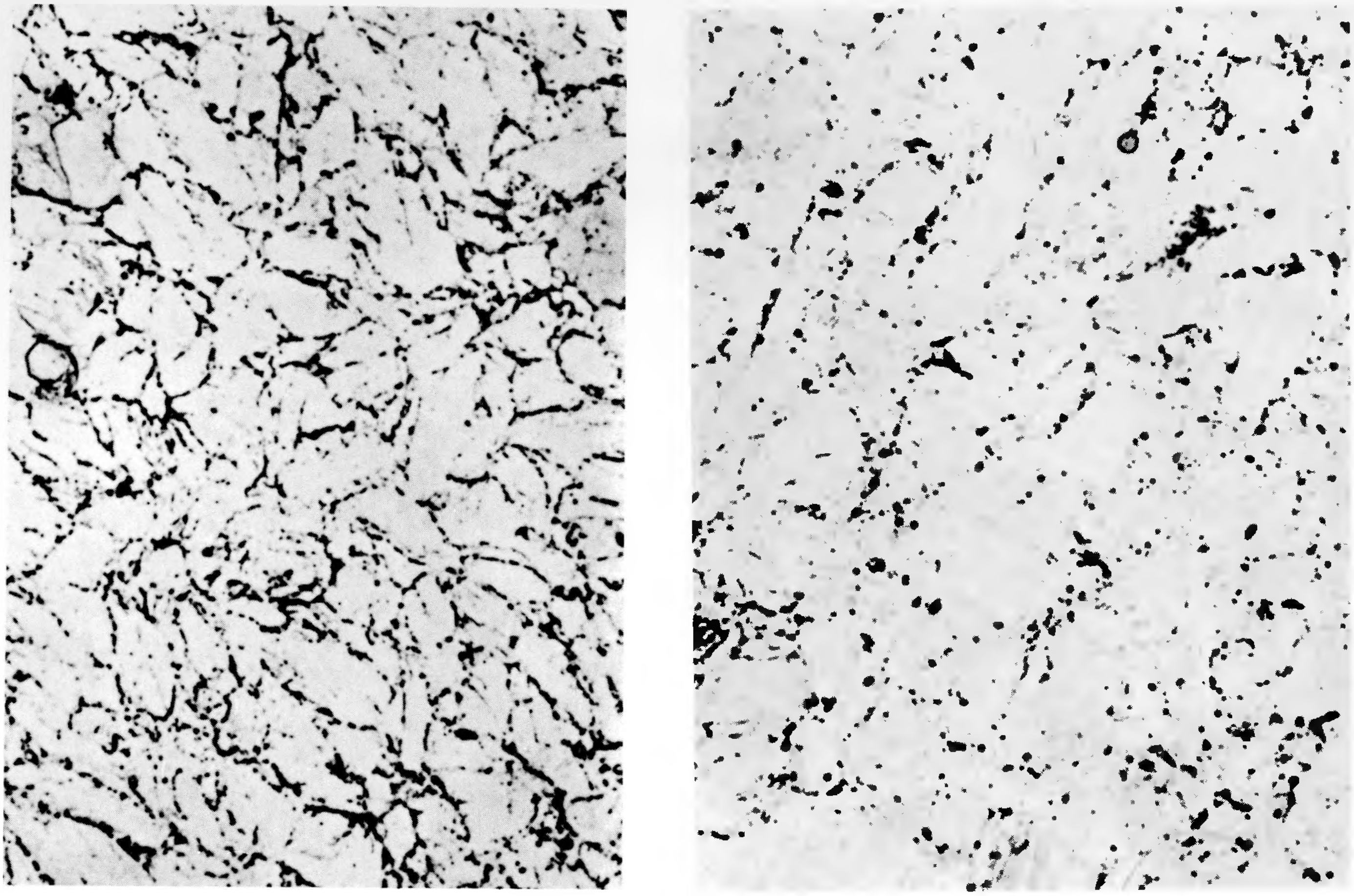


Fig. 10 - Apparatus used to prepare high purity beryllium alloy castings.



250X A-4259-4C

(a)

Hot-pressed CR-grade beryllium - 2000 ppm nickel + 2000 ppm iron, as compacted. Etchant: 1 ^{v}/o hydrofluoric acid.

250X A-4260-b

(b)

Same compact as (a), heat treated 24 hrs. at 1093°C. Etchant: 1 ^{v}/o hydrofluoric acid.

Fig. 11