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STRENGTH AND CORROSION RESISTANCE OF SOME
BERYLLIUM-BASE ALLOYS AT ELEVATED TEMPERATURE

by

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The elevated-temperature mechanical properties of beryllium have been enhanced by forming dispersed-phase alloys. The addition of properly dispersed BeO to beryllium in quantities of 2 to 3% is equivalent to lowering the testing temperature 200° in the range of 1000 to 1350°F. Similarly dispersed intermetallic compounds such as FeBe₁₁ result in a threefold increase in strength in the 1350 to 1650°F range when 1.5 to 3% iron powder is blended with beryllium powder prior to fabrication.

Tensile and stress-rupture properties of some of these materials are presented along with oxidation characteristics in 1650°F air and corrosion behavior in 600°F water relative to unalloyed beryllium.

INTRODUCTION

Certain mobile reactors now being considered include beryllium reflectors and, in some cases, moderator bodies in their design. As the operating temperatures of these reactors are increased, the elevated-temperature strength and corrosion resistance of beryllium metal become increasingly important. Accordingly, the current AEC beryllium development program includes the study of means of enhancing the elevated-temperature properties of beryllium metal.

The current investigation includes two approaches to the problem of elevated-temperature strengthening of beryllium, namely, the introduction of hard, refractory compounds into the grain-boundary area and the addition of intermetallic phases into both the grain-boundary area and, if possible, into the internal structure of the grains. While the aim of this work is primarily to increase the

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strength of beryllium, it is also necessary to maintain or, preferably, to improve the corrosion characteristics of the metal. This paper is a brief summary of progress in these endeavors to date.

STRENGTHENING OF BERYLLIUM WITH REFRACTORY COMPOUNDS

The introduction of refractory compounds such as beryllium oxide, beryllium carbide, or beryllium nitride into beryllium in quantities of 3 to 20% as strengthening agents has been investigated at the Brush Beryllium Co.¹ These materials were prepared by blending the appropriate quantities of beryllium powder and the refractory compound or fine-grained carbon in the case of the carbide and hot pressing the mixture at 2200°F (1200°C) with 2,000 psi. While full density was not reached with any of these materials under the fabrication conditions which represent the maximum temperature for beryllium and the maximum practical pressure with the present-day mold materials at this temperature, an increase of about 50% in the short-time ultimate tensile strength was obtained with beryllium carbide and about 20% was gained with beryllium nitride. Beryllium oxide added in this manner exhibited little advantage at the 3% level and actually gave lower strength at the 5% composition.

Since one of the more important requirements of a new high-strength beryllium material is that it be capable of being fabricated on a production basis, the addition of smaller quantities of the strengthening compound dispersed as widely as possible to allow conventional fabrication is now being investigated. The results obtained thus far are illustrated in Fig. 1, which shows the yield strengths of hot-pressed beryllium containing 2 and 3% BeO at temperatures between 800 and 1350°F. These bodies were fabricated in standard production equipment using powder containing the indicated amount of BeO primarily as an oxide film in order to aid dispersion of the refractory compound. It will be noted that the addition of 3% BeO in this manner results in a material as strong at 1000 and 1200°F as the normal QMV is at a test temperature 200°F lower on the basis of short-time tensile testing. The tensile-elongation pattern of these materials was not significantly different from that of QMV material. Compressive yield strengths were determined also, with almost identical values over this temperature range.

One-hundred-hour stress-rupture values, as shown in Fig. 2, indicate that the short-time advantages observed in tensile testing are retained with longer term testing even up to 1500°F. A gain of about 150 to 200°F in the strength pattern of beryllium is again indicated by these data in the temperature range of 1000 to 1500°F by the 3% BeO material.

While the usefulness of beryllium strengthened by dispersed BeO may still be restricted to maximum temperatures in the neighborhood of 1350°F, metal strengthened by properly dispersed beryllium carbide

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or beryllium nitride may offer promise at even higher temperatures, and further work is proceeding along these lines.

STRENGTHENING OF BERYLLIUM WITH INTERMETALLIC COMPOUNDS

The second approach to the problem of obtaining increased strength in beryllium above 1000°F involves the addition of intermetallic compounds between beryllium and a transition element such as iron. The materials are prepared by blending appropriate amounts of beryllium and the powder to be reacted and hot pressing in the conventional manner, again using standard production equipment, although the pressure requirements to reach full density are somewhat higher. Reaction between the beryllium and the additive material occurs during the pressing operation.

Beryllium-iron alloys prepared in this manner were found to contain only two major phases by X-ray diffraction, beryllium and the compound FeBe_{11} , which is consistent with the Fe-Be constitutional diagram published by Teitel and Cohen of MIT.² It has been noted that the intermetallic phase occurs both in the grain boundary and as oriented structures within the grain. The mechanism of this penetration has not been established, but either precipitation from a high-temperature solid solution or diffusion mechanisms could be involved.

The result of such additions on the elevated-temperature strength of beryllium in the temperature range of 1100 to 1650°F is illustrated by Fig. 3. The fabrication sequence of the materials shown here differed from the usual production sequence in that extrusion billets of the indicated composition were sintered from the powder blend at 1200°C (2200°F) under vacuum, after which hot extrusion was carried out at 1100°C (2200°F) by the conventional procedure. The values reported for QMV beryllium were obtained from material fabricated in similar fashion. The compositions shown in Fig. 3, 1.5% Fe, 1.5% stainless steel, and 2.2% Fenimo, are representative of a number of binary and ternary additions including nickel and chromium as well as iron which have been made to beryllium in quantities ranging from 1/2 to 8% by weight. Both types 302 and 410 stainless steels have been used as alloying agents, giving essentially the same results. The Fenimo material used in this work is a ferro-alloy containing approximately 49% Fe, 49% Ni, and balance molybdenum, obtained from the Pyron Corporation of Niagara Falls, New York. In general, maximum strengthening has been obtained with additions in the 1.5 to 3% range, with only a slight increase in strength values at the 3% level over the values for the 1.5% additions. As the nuclear properties and the fabrication characteristics both deteriorate with increasing amounts of additive, a balance must necessarily be struck between strengthening and the amount of additive used. At the present time this balance appears to lie in the 1.5 to 2% additive region.

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Figure 4 is a comparison of the yield strength of the 2.2% Fenimo material with that of QMV beryllium in the temperature range of 1350 to 1650°F. The impressive feature of this data is that the alloy material exhibits a yield strength at 1500°F superior to that of QMV beryllium at 1200°F. At each of the test temperatures, the alloy strength represents at least a threefold increase over the strength of the QMV material on the basis of these short-time tensile tests.

Data on the long-term strength characteristics of alloys of this type are not available as yet, but 100-hour stress-rupture values are currently being determined on several of these materials.

By way of summary, the indication at the present time is that while normal QMV beryllium may be limited to service temperatures of 1200°F or below, the addition of properly dispersed BeO may increase the service temperature under stresses of the same magnitude to 1350°F, while the addition of an intermetallic phase, such as FeBe₁₁, may increase the service temperature to 1500°F or higher. This investigation is continuing.

CORROSION RESISTANCE OF BERYLLIUM-BASE ALLOYS

While the strengthening of beryllium for elevated-temperature service is of importance, knowledge of the corrosion behavior of beryllium itself and any new alloys is also important. To date, little corrosion testing of the QMV reactor-grade metal has been carried out, most of the available data, particularly in the field of high-temperature water corrosion, being derived from vacuum-cast metal of various origin or early powder-metallurgy grades not necessarily representative of metal in service today. Thus, while a prime objective in this work has been the comparison of some of the corrosion properties of strengthened beryllium with those of the standard QMV material, study of the base characteristics of beryllium itself has been necessary.

A. Oxidation Resistance at 1650°F

In view of projected uses for the metal, its oxidation characteristics are rather important. The work of Gulbransen and Andrew³ has shown that beryllium is relatively stable towards oxidation by air to temperature of about 800°C (1470°F) on short time exposure. The effect of additives upon this oxidation resistance, however, has not been determined heretofore as far as is known. Therefore a number of beryllium alloys have been tested at 1650°F (900°C) for a period of 4 hours in dry, static air in order to determine their relative behavior. For convenience, individual specimens in the form of rounds having a total surface area of about 9 cm² were exposed to give either three or four points from which a parabolic rate constant could be calculated. Figure 5 illustrates weight gain in micrograms/cm² as a function of time for QMV beryllium and metal

containing 3% dispersed BeO. The parabolic rate constant determined for QMV beryllium from this curve lies intermediate of the two previous determinations of Cubicciotti⁴, 3.6×10^{-11} (g/cm²)²/min, and Gulbransen and Andrew³, 14.3×10^{-11} , at 5.8×10^{-11} . The previous determinations were in dry oxygen, however.

It will be noted that beryllium containing dispersed oxide exhibits an oxidation rate slightly higher than the QMV material. This has not been satisfactorily explained as yet, but it is possible that some open porosity remained in these samples even though they were above 98% of theoretical density. Densities below 98% of theoretical for a given material showed greatly increased oxidation rates.

Table I summarizes the behavior of alloy materials relative to that of QMV beryllium under the same testing conditions and during the same test period. The rate is calculated by dividing the parabolic rate constant of the alloy material by the rate constant of QMV beryllium.

These data indicate that iron, nickel, silicon, and aluminum tend to lower the oxidation rate of beryllium at 1650°F, with aluminum and silicon appearing the most promising. The excellent results obtained in one series of tests with silicon were not duplicated, however, on a second test, nor were these results duplicated with materials containing larger amounts of silicon, indicating that the establishment of a protective BeO-SiO₂ layer is not a function of composition alone if this be the mechanism.

The practical value of such beneficiation of the oxidation characteristics of beryllium, of course, remains to be determined by longer term tests at actual use temperatures.

B. Corrosion by 600°F Water

Data reported for the resistance of beryllium to high-temperature water are particularly inadequate and controversial in nature, the results ranging from the almost complete destruction of samples at 525 and 600°F in water after about seven days to rather good corrosion rates at these temperatures. In every case, however, the testing has been limited in nature or did not involve present-day metal.

Accordingly, an effort is currently being made to define the corrosion behavior of beryllium in elevated-temperature water. For the initial work, an attempt has been made to isolate metallurgical variables by using samples prepared in a standard manner and to concentrate on environmental effects. The samples were isolated from galvanic coupling by the use of BeO insulators. The samples were flats approximately 1 in. wide by 1 3/4 in. long by 1/8 in. thick with a 1/4-in. hole drilled in one end for suspension on the BeO. Surface treatment consisted in machine grinding to about 32 micro-

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TABLE I

RELATIVE OXIDATION RATES OF BERYLLIUM-BASE
ALLOYS IN STATIC AIR AT 1650°F (900°C)

<u>Material</u>	<u>Relative Rate</u>
QMV	1.0
1% Ni	0.7
5% Ni	0.6
10% Ni	0.9
1/2% Fe	1.0
1% Fe	1.2
1 1/2% Fe	0.8
3% Fe	0.7
6% Fe	0.7
3% Cr	1.2
1/2% Si	0.3-1.1
1% Si	1.1
5% Si	1.2
9% Si	0.7
2% Al	0.5

$$\text{Relative Rate} = \frac{\text{Wt. gain/cm}^2\text{-min}^{1/2} \text{ alloy}}{\text{Wt. gain/cm}^2\text{-min}^{1/2} \text{ QMV}}$$

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inches followed by degreasing with acetone and drying prior to weighing. The autoclaves used for this testing were standard 1-gallon stainless steel units, with the sample suspension being accomplished from an inserted stainless steel basket.

Table II gives a summary of data gathered to date on the behavior of QMV beryllium in deionized water at 600°F (specific resistance 18×10^5 ohm-cm or more). The corrosion rate values were calculated on the basis of total weight gain after the indicated test period, the sample then being tested in fresh water for additional time until 28 days was reached. The accuracy of this procedure was checked in several instances by defilming the sample after 28 days in a dilute chromic-phosphoric acid solution and calculating the weight gain from the defilmed weight. A variance of only about 5% from the actual weight gain was obtained.

The observed corrosion rates rapidly decrease with time during the first 28 days at 600°F, as indicated in Table II, until at the 28-day point, values of about the same order of magnitude as Zircalloy-2 are obtained. The data tend to indicate that even lower rates are possible if the testing were carried out continuously during the 28-day period as the last two materials exhibit lower rates, the major difference being uninterrupted testing during the first 7 days. The fabrication sequence is apparently not significant here because hot-pressed material carried as controls in alloy tests to be described later behaved in similar fashion. While the values shown are the average for three samples in most cases, the total range of corrosion rate after 28 days was 11.3 to 20.8 mdm, which is very close to the average range. No pitting attack was observed on these samples.

While these results seem very encouraging for beryllium in high-temperature water, several factors have been found which have a severe effect upon the resistance of beryllium to high-temperature water. The most important of these appears to be water purity. The introduction of 20 ppm of chloride ion results in severe pitting of the metal and even disintegration of the sample after only 7 days; 2 to 3 ppm of chloride will not necessarily pit the samples, but the corrosion rate after 28 days will be two to three times that otherwise observed. It has also been noted that the density of the sample is very important, densities below 98% of theoretical giving apparent corrosion rate values as high as 1 or 2 magnitudes greater than the corresponding full-density material. This is possibly due to connected porosity in such samples.

Table III compares the behavior of a number of beryllium-base alloys in 600°F water during 28-day tests. Since some of these tests were carried out with interruption after different test periods, the comparison is made on the basis of a factor calculated by dividing the alloy rate by the rate of a QMV control carried in the same test

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TABLE II

CORROSION RATE OF QMV BERYLLIUM IN 600°F DEIONIZED WATER
AS A FUNCTION OF EXPOSURE TIME
(mg/dm²-mo)

<u>Lot No.</u>	<u>After 1 Day</u>	<u>After 4 Days</u>	<u>After 7 Days</u>	<u>After 14 Days</u>	<u>After 28 Days</u>
Y-5744 VHP	+195	+62	+44	+30	+20
Y-5802 VHP	+280	+78	+44	+31	+19
Y-5906 VHP	+224	+72.6	+44	+38	+19
Y-5573 VHP-HX	---	---	+31	+18	+12
Y-5486 VHP-HX	---	---	+31	+23	+11

∞

Range of samples after 28 days +11.3 to +20.8 mdm.

TABLE III

CORROSION RATE OF BERYLLIUM-BASE
ALLOYS IN 600°F DEIONIZED WATER

QMV Beryllium (28 Day Exposure) +11.3 to +20.8 mdm		
<u>Material</u>	<u>Test Time</u>	<u>Rate Relative to QMV in Same Test</u>
2% BeO	28 days	1.1
3% BeO	28	1.3
1/2% Fe	28	2.2
1% Fe	28	1.7
1 1/2% Fe	28	1.5
3% Fe	28	2.1
1 1/2% Stainless	28	1.6
3% Stainless	28	1.7
3% Cr	28	1.3
10% Ni	12	1.1
2% Zr	12	1.2
1/2% Si	28	1.0
2% Si	12	Catastrophic
9% Si	28	Severe pitting
1% Al	12	Catastrophic

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after the 28-day test period. In no case was a corrosion rate superior to that of QMV beryllium obtained. A number of alloys, including the BeO compositions, the 3% Cr, 2% Zr, and 10% Ni materials, were essentially comparable to the QMV metal. The iron-containing alloys exhibited a somewhat higher rate generally, but were still considered good as 28-day rates under 20 mdm were obtained in some cases.

It was observed, however, that aluminum and silicon were apparently quite detrimental to the corrosion resistance of beryllium under these conditions. Aluminum results in severe weight loss and generalized attack, while silicon renders the metal susceptible to pitting attack as indicated in Table III. Figure 6 illustrates these two types of attack.

It is planned to test the resistance of these materials to attack by molten sodium, but no data are available at the present time.

SUMMARY

The work has shown to date that beryllium may be appreciably strengthened in the temperature range of 1000 to 1350°F by the addition of about 3% BeO in a properly dispersed manner while retaining the ability to be fabricated by standard methods. The addition of iron, in quantities of 1.5 to 3 wt.% to form the compound, FeBe₁₁, in the structure of the metal has resulted in even greater strengthening of beryllium; strengths as high as three times that of QMV at temperatures in the range of 1350 to 1650°F have been obtained. The water-corrosion and air-oxidation characteristics of such materials are comparable to those of beryllium, if not more favorable. It is felt that continued work in this field will bring about the preparation of materials of even more promising characteristics for high-temperature service.

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FIGURE I

EFFECT OF BeO ADDITIONS ON YIELD STRENGTH OF
VACUUM HOT-PRESSED BERYLLIUM

FIGURE II
100 HOUR STRESS-RUPTURE STRENGTH OF BERYLLIUM
AS A FUNCTION OF BeO CONTENT

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FIGURE III

ELEVATED TEMPERATURE, ULTIMATE TENSILE
STRENGTH OF SOME BERYLLIUM-BASE ALLOYS

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FIGURE IV

EFFECT OF 2.2% FENIMO ON ELEVATED TEMPERATURE
YIELD STRENGTH OF BERYLLIUM

FIGURE V
 OXIDATION BEHAVIOR OF BERYLLIUM
 AT 1650°F IN STATIC, DRY AIR

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FIGURE VI

EFFECT OF COMPOSITION ON CORROSION RESISTANCE
OF Be. LEFT: 1% Al ALLOY AFTER 14 DAYS IN 600°F
H₂O. CENTER, PITTED 9% Si ALLOY AFTER 28 DAYS IN 600°F
H₂O. RIGHT: STANDARD QMV Be AFTER 28 DAYS IN 600°F H₂O

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