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DMIC Report 242
December 11, 1967

CORROSION OF BERYLLIUM

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DMIC Report 242
December 11, 1967

CORROSION OF BERYLLIUM

BY

P. D. Miller and W. K. Boyd

to

**OFFICE OF THE DIRECTOR OF DEFENSE
RESEARCH AND ENGINEERING**

**DEFENSE METALS INFORMATION CENTER
Battelle Memorial Institute
Columbus, Ohio 43201**

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CORROSION OF BERYLLIUM

P. D. Miller and W. K. Boyd*

SUMMARY

Beryllium is sufficiently corrosion resistant to be of great usefulness in many engineering applications. Its resistance to most environments is similar to but somewhat less than that of aluminum, which certainly is being widely used. This report indicates areas in which corrosion may be anticipated. In general, the response of beryllium to acidic and alkaline solutions is much like that of aluminum. It is more sensitive than aluminum to impurities such as chlorides, sulfates, and fluorides in water, so all handling and cleaning must be carefully done. For example, contact with tap water should be avoided in most instances. The resistance to high-purity water, however, is quite good. Extensive pitting occurs in seawater.

Organic solvents such as methyl alcohol or methyl ethyl ketone in combination with water, Freon, or perchlorethylene react quickly with beryllium. Hydrocarbon solvents are probably to be preferred.

The chemical resistance of beryllium, like that of aluminum and titanium, is due to a tightly adhering oxide film. This oxide coating is protective and stable in air at temperatures up to about 1200 F. The protection is lost at higher temperatures and the oxidation becomes catastrophic.

Beryllium is fairly resistant to most liquid metals except aluminum and possibly calcium. Temperature levels and metal purity, however, are of great importance here. It is quite resistant to molten sulfur.

No failures from stress-corrosion cracking have been reported for beryllium. However, most studies in this area have been made in salt solutions in which excessive pitting occurred so that the exact cause of rupture could not be clearly established.

Beryllium is anodic in most galvanic couples, and bimetallic systems wet with conducting solutions should be avoided.

Anodic and chemical conversion coatings are very beneficial in improving the corrosion resistance of beryllium in both aqueous and gaseous environments. Metallic coatings have also proven valuable.

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INTRODUCTION

The interest of the U. S. Air Force, NASA, and the U. S. Navy in structural applications of beryllium metal has spawned a fairly extensive technology. Research has centered on areas that will help exploit the unique properties of the metal. For example, it is relatively light and has an extremely high modulus of elasticity, good mechanical strength, and high heat capacity with good thermal conductivity.

The corrosion resistance of structural materials is of great importance in all engineering developments. This report draws together the data summarizing the general corrosion behavior of beryllium and its alloys in various gases, salt solutions, mineral acids, organic compounds, and liquid metals.

The report supplements other data on beryllium as set forth in reports from the Defense Metals Information Center as follows:

DMIC Report 168, Beryllium for Structural Applications, 1958-1960, May 18, 1962, (AD 278723).

DMIC Memorandum 198, Surface Damage in Machined Beryllium, January 4, 1965, (AD 610709).

DMIC Memorandum 197, Electrodeposited, Electroless, and Anodized Coatings on Beryllium, September 1, 1964, (AD 609132).

DMIC Memorandum 183, The Current Status and 1970 Potential for Selected Defense Metals, October 31, 1963 (AD 425604).

DMIC Memorandum 138, Review of Recent Developments in the Technology of Beryllium, November 16, 1961 (AD 267079).

DMIC Memorandum 123, Review of Recent Developments in the Technology of Beryllium, August 18, 1961 (AD 262497).

DMIC Memorandum 105, Review of Recent Developments in the Metallurgy of Beryllium, May 10, 1961 (AD 256206).

DMIC Memorandum 37, Procedures for the Metallographic Preparation of Beryllium, Titanium, and Refractory Metals, October 26, 1959, (PB 161187).

DMIC Memorandum 36, Heat Capacity of Beryllium, October 19, 1959 (PB 161186).

DMIC Memorandum 21, Machining of Beryllium, June 5, 1959 (PB 161171).

DMIC Memorandum 13, Joining of Beryllium, March 30, 1959 (PB 161163)

DMIC Memorandum 2, Some Notes on Safe Handling Practices for Beryllium, September 22, 1958 (PB 161153).

Useful information on beryllium can also be found in DMIC Reviews of Recent Developments on Beryllium for June 2, 1967; September 23, 1967; March 1, 1967; December 30, 1966; February 4, 1966; November 5, 1965; August 11, 1965; May 21, 1965; February 26, 1965; November 6, 1964; and May 8, 1964.

CORROSION RESULTS

General Nature of Beryllium

Beryllium is the only alkaline earth metal for which the oxide has a volume ratio of oxygen to metal that is greater than unity, i. e. , 1.68. Thus, the oxide can be protective and in this respect beryllium resembles metals more to the right and lower in the periodic table, i. e. , aluminum, titanium, zirconium, etc. In general, the corrosion resistance of beryllium is similar to that of aluminum in many environments. It combines readily with oxygen and nitrogen, and these reactions are discussed in detail in later sections of this report.

Effect of Impurities

Reported corrosion results for beryllium often do not seem to be consistent or reproducible. There are indications that these variations are at least in part caused by differences in metal purity. As pointed out by Bunshah, commercial beryllium contains many impurities. (1) Some of these are in solid solution and others are as dispersed phases. Impurities in normal commercial grades vary from 1 to 4.5 percent. The major impurities are O₂, C, Fe, Cr, Ni, Si, Al, and Cu. The amounts of these impurities found in various grades of beryllium are listed in Table 1, which is a composite from Reference (1). Common commercial material contains a maximum of 2.0 percent BeO. The Beryllium Corporation of America refers to beryllium of this grade as HP20, the Brush Beryllium Company as S-200, and General Atomics Corporation as GB-2. Instrument-grade material I-4C0 assays only 92 percent beryllium.

As pointed out by Stonehouse, beryllium carbide, Be₂C, is present in all commercial metal in amounts in the range 1000 to 1500 ppm. (2) This carbide reacts with moisture, and is slowly converted to beryllium oxide and methane. Thus, any large carbide inclusions could cause difficulties in corrosion-behavior characteristics of beryllium. It is also pointed out that aluminum and silicon, as well as other impurities, can adversely affect the resistance of beryllium to aqueous corrosion.

TABLE 1. PURITY AND PRINCIPAL IMPURITIES IN VARIOUS FORMS OF BERYLLIUM
(Beryllium in percent, impurities in parts per million) (Reference 1)

Element	Pechiney Flake	Hot- Mg- Pressed		Electro- lytic Flake (Comm. Grade)	Vacuum- Melted Ingot (BeO Crucible)	Electro- lytic Flake, Super-Pure (SR Grade)	Vacuum-Distilled Beryllium	
		Reduced Pebble	Powder (QMV)				Nuclear Metals, Inc.	USSR
Be	99.5	98.5-98.8	98.9	99.4	~99.4	~99.9	~99.99	99.98 (not counting O ₂ and C)
O ₂	2,300	4,000	9,700	4,000	2,000	300	100	100-200
C	300	450	900	300	400	300	N. D. (a)	100
N ₂	--	100	100	50	100	N. D. (a)	N. D. (a)	N. D. (a)
Fe	300	700	1,220	300	1,500	<20	3	10
Cl	1,000	50	--	1,100	--	400	--	--
Cr	20	90	140	25	300	<100	1	30
Mn	60	90	90	100	130	60	5	10
Ni	150	80	100	200	300	<20	2	1
Si	75	550	300	300	250	90	12	20
Al	<200	500	500	300	500	<50	20	20
Mg	50	6,000	80	50	150	5	--	10
Cu	--	27	150	100	30	<20	5	5

(a) Not detected.

Because of the progressive improvements in the quality of beryllium available, this report emphasizes the more recent corrosion literature on the assumption that these results represent more accurately the true status at this time.

Environmental Compatibility

Cold Water

Beryllium has excellent corrosion resistance in low-temperature, high-purity water. For example, Stonehouse and Beaver report that corrosion has not been a problem during 10 years of operation of a nuclear test reactor using demineralized water at a pH of 5.5 to 6.5. (2) In addition, accelerated corrosion of beryllium was not observed in this environment, even when the beryllium was coupled to stainless steel or aluminum. In general, the corrosion rates in good-quality water are less than 1 mpy (mils per year). (3)

Beryllium, however, is much less attractive for use in water containing ionic impurities, particularly chloride and sulfate ions. For example, it is often corroded by tap water. The attack usually takes place by pitting. Thus, any expression of an overall corrosion rate in units such as mils per year must be correlated with observations of the pit depth. Details on the status of aqueous corrosion up to about 15 years ago are given by White and Burke (4) and up to 1960 by Darwin and Buddery. (5)

Some estimate of the chemical resistance of beryllium to electrolytes can be obtained from the equilibrium potential - pH diagram developed by Pourbaix (6) and reproduced in Figure 1. It must be remembered, however, that this diagram represents standard state conditions and ionic concentrations of 10^{-6} . A solution is assumed to be corrosive or not, according to whether the quantity of metal it tends to dissolve is more or less than 10^{-6} gram-atom per liter.

Humid Air

An extensive corrosion study in water vapor was reported by Gilpin and Mackay. (7) They used specimens made from hot-pressed blocks containing about 3 percent BeO. Polished, bare coupons, along with coupons coated by various materials, were exposed for 30 days to 95 percent relative humidity at 100 F. Neither microscopic examinations nor weight-gain measurements indicated corrosion on any of the pieces. Further details of their study are given in later sections of this report.

Hot Water

At the present time, the corrosion behavior of beryllium in high-temperature water and in steam up to 752 F and 1500 psi is variable, and depends on a number of factors including metal purity, surface preparation, and environmental conditions. Kneppel found that high-purity beryllium prepared by distillation and/or zone refining, and commercial high-purity beryllium corrode catastrophically within about 2 days in water at 650 F. (8)

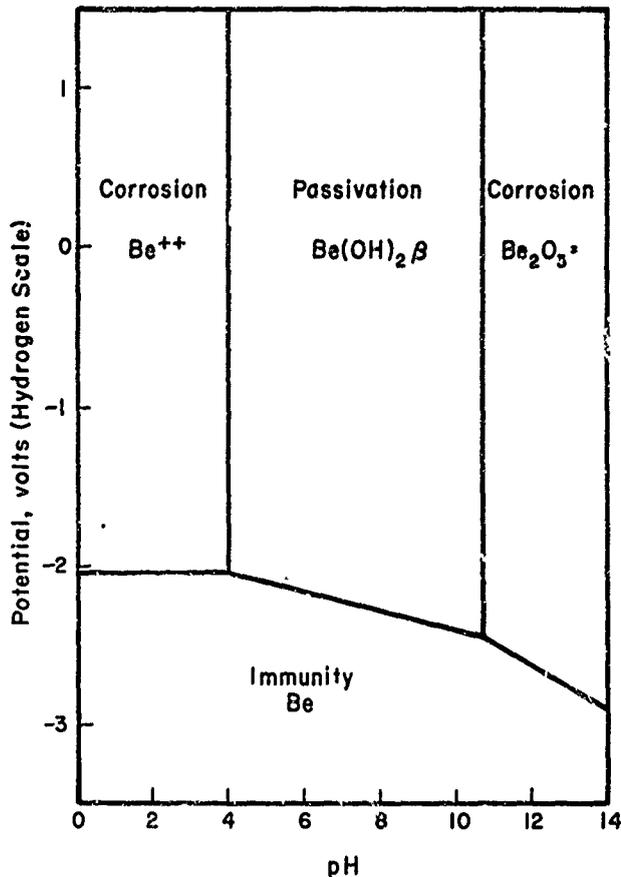


FIGURE 1. EQUILIBRIUM POTENTIAL - pH FOR THE SYSTEM BERYLLIUM - WATER AT 77 F(6)

Alloy additions of nickel or combinations of nickel and iron (4000 ppm Ni, 2000 ppm Ni-2000 ppm Fe, or 5000 ppm Ni-5000 ppm Fe) greatly improved the corrosion resistance of high-purity beryllium. For example, specimens made from alloyed Pechiney CR-grade powder showed no signs of attack for times up to 43 days in water at 650 F. The beneficial effect from nickel was not confirmed by Stonehouse and associates. (2)

Additional research will be required to clarify the cause of the unpredictable behavior of beryllium. There is some indication that it is related to the presence of small amounts of copper contamination in the water. General results can be summarized as follows:

- (1) Specimens with acid etched surfaces were less corrosion resistant than those not etched.
- (2) Mechanical removal of more than 12-14 mils of the outer surface also rendered the specimens less corrosion resistant.
- (3) Localized boiling on specimen surfaces increased the corrosion rate.

Beryllium specimens exposed to steam at 752 F at 1500 psi were attacked in much the same manner as those in water at 650 F. The localized attack in steam was somewhat more severe.

Salt Solutions

As was mentioned in an earlier section, beryllium is subject to pitting attack in aqueous environments containing chloride ion. Intermittent immersion tests conducted by Prochko and associates^(9,10) at ambient temperatures (about 60 F) and 30 days of exposure indicated overall corrosion rates and penetrations listed in Table 2. Corrosion-test specimens were prepared from cross-rolled, surface-ground, flash-pickled (HF-HNO₃) sheet. The 60-mil beryllium sheet of commercial purity assayed 98.3 percent Be, 1.63 percent BeO, and 0.113 percent carbon.

Figure 2 shows the weight losses and penetrations for the specimens in the five test solutions after intermittent exposures.

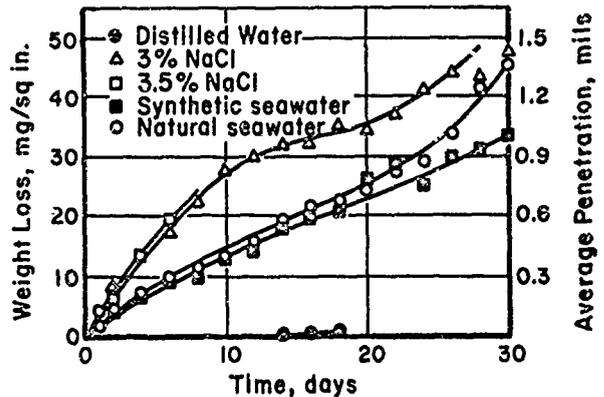


FIGURE 2. CORROSION OF PICKLED BERYLLIUM SHEET IN FIVE ENVIRONMENTS (Intermittent total immersion testing was conducted using these selected chloride solutions at 60 F. (Reference 9)

Exposures at 60 F and 95 F showed that the corrosion rate increased as the temperature was raised. For example, after 14 days of intermittent total immersion in natural seawater the rates for the above temperatures were 17.1 and 25.9 mpy, respectively. By comparison, the corrosion rate for anodized beryllium was only 0.3 mpy after 60 days in seawater.

The corrosion rates decreased with time of exposure for samples exposed continuously at 60 F in natural seawater. Results are summarized in Table 3.

A later report from the same laboratory indicates that the corrosion rate of beryllium in synthetic seawater decreases from about 21.2 mpy at 5 days' exposure to about 3.0 mpy at 150 days. (11) Figure 3 illustrates these results.

TABLE 2. CORROSION OF BERYLLIUM IN SALT SOLUTIONS AT 60 F (Reference 9)

Environment	Overall Corrosion Rate ^(a) , mpy	Max Pit Depth, mils
Distilled water	0.8	0.8 ^(b)
Synthetic seawater	13.7	4.6
Natural seawater	18.4	4.6
3% NaCl solution	21.5	--
3.5 NaCl solution	33.4	6.8 ^(c)

(a) 30 days.

(b) 18 days.

(c) 8 days.

TABLE 3. CORROSION IN NATURAL SEAWATER AT ABOUT 60 F

Continuous total immersion. (Reference 9)

Time, days	Corrosion rate, mpy	Max Pit Depth, mils	Percent of Surface Pitted
2	--	1.5	Negligible
5	--	1.6	1
20	13.0	3.0	5
30	10.5	3.0	12
40	9.0	2.5	15
60	6.5	3.0	20
182(a)	2.4	--	--

(a) Extrapolated value.

It should be pointed out that the maximum pit depth also increased in a similar manner from about 1.6 to 3.2 mils as the exposure time increased from 5 to 150 days. A summary of the results concerning pitting is given in Figure 4. It can be noted that the percentage of the surfaces pitted increased linearly from about 2 to 45 percent as the exposure period increased from 5 to 150 days.

In work at Battelle, a very low general rate of attack was found for beryllium in seawater, but evidence of possible pitting was also observed. The beryllium was exposed in aerated seawater (except for a period of about 6 hours a day, for 5 days a week, when it was suspended above the water). After 2 weeks' exposure, the corrosion rate was equivalent to 3.6 mpy. The surface appeared to be coated with a white powder, probably BeO, and had small-size clear hydroscopic bubbles on its surface. Underneath these bubbles some pitting was found.

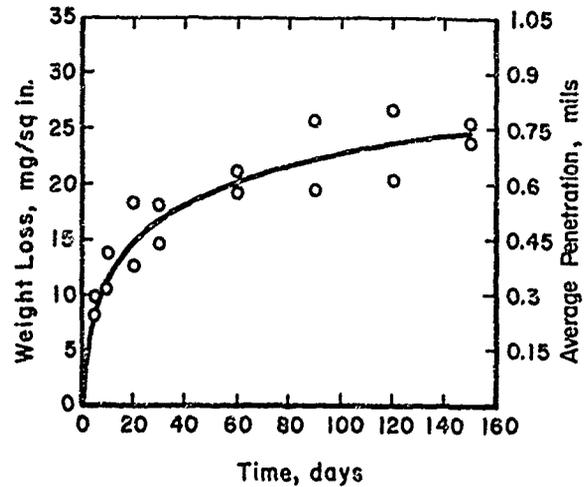


FIGURE 3. CORROSION OF UNSTRESSED, PICKLED BERYLLIUM SHEET MATERIAL EXPOSED TO SYNTHETIC SEAWATER AT 77 F (Continuous total immersion testing. Reference 11).

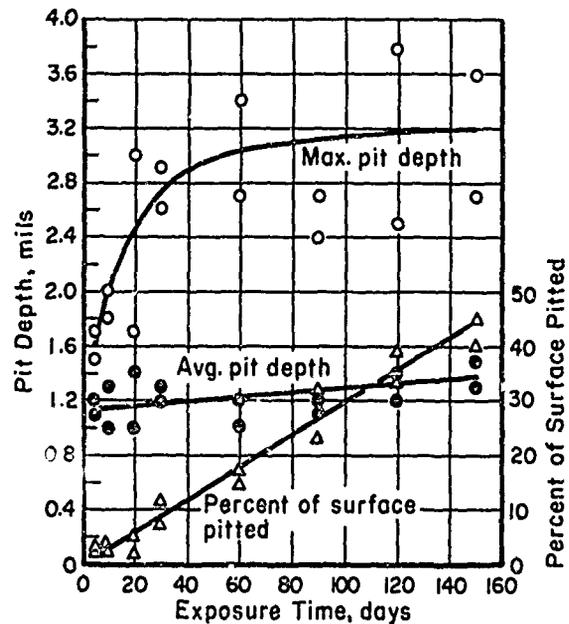


FIGURE 4. PITTING ATTACK OF UNSTRESSED, PICKLED BERYLLIUM SHEET MATERIAL EXPOSED TO SYNTHETIC SEAWATER AT 77 F (Continuous total immersion testing. Reference 11).

Workers at Astropower exposed bare beryllium (nominal 2 percent BeO content) specimens alternately to a 5 percent salt solution at 100 F for 16 hours, followed by air exposure at elevated temperatures up to 800 F for 8 hours. (7) Tests were continued for a total of 14 cycles. The specimens were first attacked at localized areas (pitting). The maximum corrosion resistance was found at 600 F and was attributed to the formation of a protective oxide film.

It is pointed out, however, that corrosion rates in such service are higher than can be tolerated, so that additional protection is required for satisfactory service life.

Salt Fog

Bare beryllium specimens (nominal 2 percent BeO content) were exposed to a 5 percent salt-fog spray at 100 F for 30 days at the Astropower Laboratory. (7) Localized pitting occurred on the bare pieces after only 1 day of exposure. The attack increased with exposure time. The specimens were rinsed in distilled water after 30 days and then were weighed. The weight loss at several time intervals is given in Table 4. The values in the last column (actual) were obtained by dissolving the corrosion product in 49 percent HNO₃ and 1 percent HF and adjusting for the bare metal dissolved. The corrosion rate corresponding to weight losses in the range shown is 2.2 mpy. Pit depths of 15 to 25 mils were measured on the coupons.

TABLE 4. WEIGHT LOSSES OF FORGED 1x2-IN. IN 5 PERCENT SALT-FOG SPRAY AT 100 F (Reference 7)

Specimen	Day	Weight Loss at Indicated Exposure Times, mg							
		1 Day	2 Days	4 Days	7 Days	14 Days	21 Days	30 Days	30 Days (Actual) ^(a)
3-4		0.33	0.50	0.90	1.6	3.8	5.6	7.3	23.1
5-4		0.42	0.7	0.89	1.2	2.5	2.7	3.1	27.2
5-5		0.40	0.7	0.91	1.1	2.0	2.4	2.9	17.6
1-1	--	0.5	0.71	0.9	1.9	2.6	3.5	22.5	

(a) (Actual) values indicate weight losses of specimens after corrosion products were stripped from coupons, and are equivalent to about 2.2 mpy.

In another study at the same laboratory, coupons were alternately exposed to a 5 percent salt fog at 100 F for 16 hours, and then immediately placed in an oven for 8 hours at 200, 400, 600, or 800 F.

The following observations were reported for polished beryllium when exposed to alternate cycles of salt-fog spray and elevated temperatures.

- (1) Chemical attack was observed on polished bare beryllium following the initial cycle at all of the above temperatures.
- (2) At 200 F the pitting observed after the first initial cycle increased with each subsequent cycle as evidenced by the increase in the number and size of the pits. The behavior at this condition is very similar to the results obtained for the 30-day, 5 percent salt-fog spray.
- (3) At 400, 600, and 800 F, the cyclic effect of temperature and salt contamination was found to proceed by two independent mechanisms.

Initially, a weight loss was observed, due to chemical attack by the salt environment. After the first few cycles, a thin oxide coating was formed, due to oxidation in air at the elevated temperature.

- (4) At 800 F, very small white oxide patches started to appear at about about the tenth cycle. At this stage the coupons started to show small weight increases. The appearance of the white oxide is indicative of the onset of the catastrophic oxidation, which is discussed later in this report.

Acids

Beryllium reacts with the halogen acids in all concentrations at room temperature. It reacts with dilute sulfuric acid readily and with concentrated sulfuric acid slowly. It is attacked by dilute nitric and acetic acids, but not glacial acetic acid or concentrated nitric acid at room temperature. With concentrated nitric acid, reaction occurs and becomes violent as the temperature is increased above room temperature.

Straumanis and Mathis report studies with premium-grade vacuum-cast metal (assaying 99.0 percent Be) in HF, HCl, and H₂SO₄. (12) The metal is removed uniformly in HF and H₂SO₄. The reaction with HCl is more localized, and a black deposit forms which has been identified as fine needles of metallic beryllium. The black deposit was not found when concentrations greater than 0.5N HCl were used.

The reaction mechanisms were checked by measuring the volume of hydrogen evolved from weight samples. It was concluded that the reactions with acids are:



Rapid attack and the formation of a black deposit were observed in HClO₄ and HBr.

It is interesting that a similar black deposit, consisting mainly of fine beryllium needles, is formed on beryllium anodes when the metal is electrolytically dissolved in a 0.5N HCl solution. (13)

Alkalies

Beryllium is vigorously attacked by aqueous alkaline solutions. Molten alkalies may react explosively with the metal.

Oxygen and Air. The thin oxide film formed on beryllium in air at ambient temperatures is quite protective, and the metal can be stored at room temperature for years without the occurrence of any noticeable change in appearance. The metal in most cases can be heated to about 1100 F in air before significant corrosion occurs. (14) At temperatures above about 1400 F the film becomes nonprotective and the metal can be converted in time to an oxide powder.

Studies made in England of the oxidation of Pechiney flake beryllium (<0.3 percent BeO) in dry oxygen showed that at temperatures up to and including 1200 F the oxide film is quite protective. (15) Actually, at temperatures below 1200 F the corrosion rate decreased continuously with time. A value of 0.013-0.026 mpy was reached at about 930 F after 300 hours. At about 1382 F the oxidation became rapid and went through two stages. This transition, in which the rate first decreased and then increased with time, is illustrated by Curves (1) and (2) in Figure 5. Most investigators in this field call

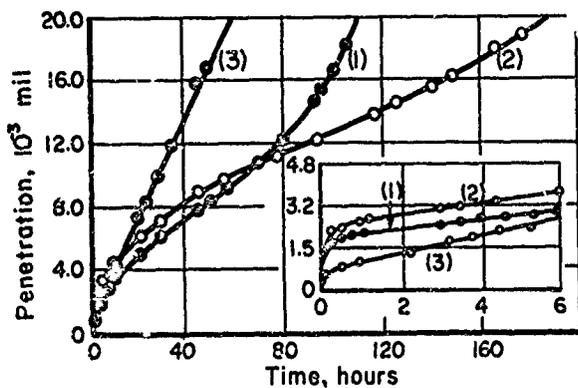


FIGURE 5. CALCULATED PENETRATION OF BERYLLIUM AT 1582 F BASED ON OXIDATION DATA (Reference 15) Dry oxygen atmosphere and weight-gain values.

the transition from protective to nonprotective oxidation a "breakaway" point.

Curve 3 in Figure 5 does not show this transition, and indicates a constant corrosion rate. It is included to illustrate the variability in results. The penetrations shown in Figure 5 were calculated from weight-gain values, and assume no localized attack. Since some cracking and healing of the film is reported, the penetration at some areas is probably greater than those given in Figure 5.

Ervin and Mackay studied the oxidation in dry oxygen over the temperature range 932-1652 F. (16) They found that for a short time the film was protective and the corrosion rate curve was parabolic. The duration of the

initial parabolic period, however, decreased with increasing temperature. The type of beryllium used was also of importance. Vacuum-cast material was somewhat more resistant than the other grades. The times at which an accelerating oxidation rate began for various temperatures with different lots of beryllium are given in Table 5.

TABLE 5. TRANSITION FROM A PARABOLIC RATE TO AN ACCELERATING RATE (Times in hours) (Reference 16)

Temperature, F	Small Single Crystals, Vacuum Distilled	Powder		Polished Specimens	
		S-200	Vacuum Cast	S 200	Vacuum Cast
1292-1382	7	30	100	150	150
1382-1472		6	25	25-100	
1472-1562	3	3	5	40	70
1562-1652			3	2	20
1652-1742	1		0	40	30

During the protective period it appears that the diffusion of beryllium-ion vacancies in the oxide film lattice controls the oxidation rate. Pitting develops in the metal beneath the protective layer and ultimately weakens and undermines both the metal surface and outer film until fracture occurs. Ervin and Mackay believe that pitting is related to dislocations and slip steps in the metal. Pits are believed to initiate at the points of emergence of dislocation lines at the metal surface. The outer layer appears to fracture as a result of stresses set up by the growing oxide film.

On the other hand, Williams and Jones believe it is possible that emergence sites of dislocations may be areas where pits initiate, but that it is very unlikely that there is a one-to-one correspondence between pits and dislocations, at least for thermal etch pits. (17)

The oxidation rates and the type of oxidation curves described by Aylmore and Associates and by Ervin and Mackay are not in agreement with those reported by Stonehouse and Beaver, (2)(18) which are shown in Figure 6. The penetrations shown in this figure are about 160 times greater than those in Figure 5. The reason for the poor agreement is not apparent.

Bennett and Associates found that irradiation of the beryllium produced helium which caused swelling of the metal (Pechiney and Brush material) specimens. (19) An increased rate of oxidation was observed because of the swelling and was explained on the basis of the increased area available for reaction.

The corrosion of QMV beryllium in air at pressures to 15 psi over the temperature range 1705-2360 F was studied by Bradshaw and Wright. (20) They found that the corrosion rate is essentially linear after a short induction period

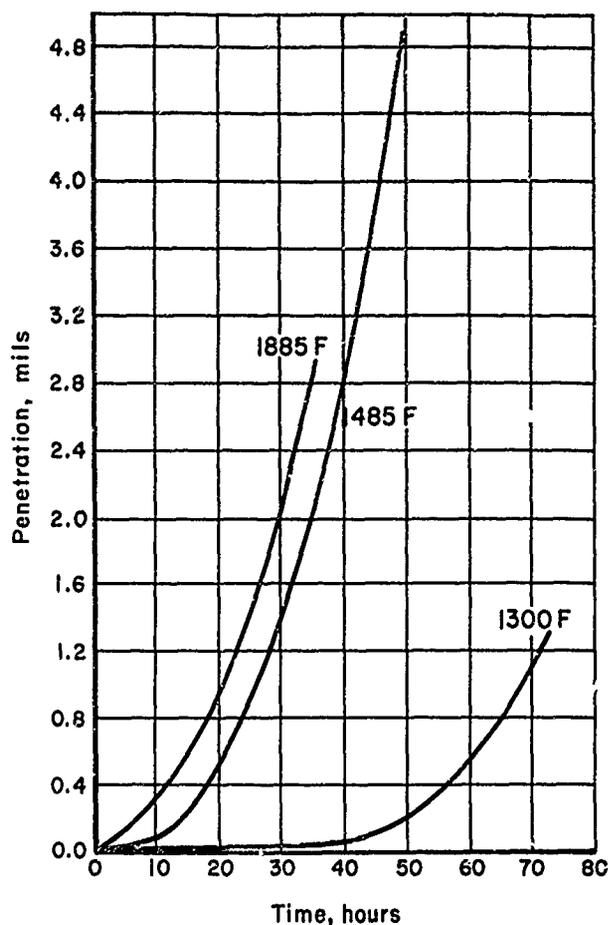


FIGURE 6. CALCULATED PENETRATION OF BERYLLIUM AT ELEVATED TEMPERATURES BASED ON OXIDATION DATA (References 2 and 18)

Dry oxygen at 1 atmosphere pressure.

and that the oxide is not protective. These investigators conclude that the reaction rate does not become extreme, assuming short-term application, until temperatures above 2190 F are reached.

An oxidizing pretreatment in phosphoric/sulfuric acid lengthens the induction period. (21) Spherical blisters form on anodized beryllium when heated in air. Such anodic coatings are discussed in more detail in another section of this report.

For some applications there is interest in the behavior of beryllium in oxygen or air at temperatures up to the melting point, 2340 F, and beyond. This point was extensively studied at TRW Systems⁽²²⁾ using QMV-grade beryllium containing 1.67 percent BeO. They found catastrophic oxidation to occur at temperatures above 1920 F, which is somewhat higher than that suggested by research described in some earlier sections of this report. The TRW group found that the reaction rate between 1920 and 2335 F was characterized by a linear oxidation

mechanism and had nearly a first-order dependence on oxygen pressure. At temperatures above the melting point the oxygen-pressure dependence was nearly half order. A specimen originally 3/16 inch in diameter and 1/2 inch long was more than 50 percent oxidized in 15 minutes at 2732 F at 1 atmosphere pressure of oxygen.

Water Vapor and Moist Oxygen. The corrosion of electrolytic flake beryllium in water vapor is about the same as in moist oxygen in the temperature range 930-1380 F according to Alymore and Associates. (23) Figures 7 and 8

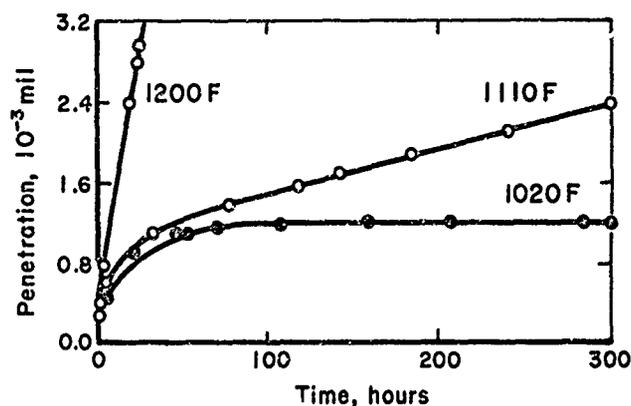


FIGURE 7. CALCULATED PENETRATION OF BERYLLIUM BASED ON OXIDATION IN WATER VAPOR AT A PRESSURE OF 1.2 CM (Reference 23)

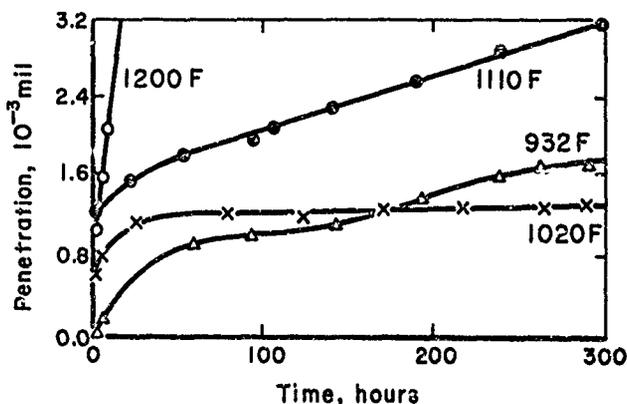


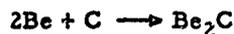
FIGURE 8. CALCULATED PENETRATION OF BERYLLIUM BASED ON OXIDATION IN MOIST OXYGEN AT A TOTAL PRESSURE OF 10 CM WITH 1.2 CM PARTIAL PRESSURE OF WATER (Reference 23)

show the comparison. The coating is protective up to and including 1112 F. It is interesting that the weight gains in this temperature region are in many ways similar to those in dry oxygen.

Rapid oxidation was experienced in water vapor and moist oxygen at temperatures above 1200 F. The attack takes the form of localized intergranular penetration of the metal.

Carbon Dioxide and Carbon Monoxide.

There has been considerable interest in the durability of beryllium in atmospheres containing CO₂ and CO from the standpoint of nuclear-reactor technology. Gregg and Associates have studied the reaction of Pechiney flake beryllium with CO₂ and CO at temperatures in the range 930-1380 F using a radioactive-tracer technique. (24,25) It was concluded that the following reactions occur:



In carbon dioxide, at temperatures up to 1292 F, the rate of oxidation decreased as exposure time increased (See Figure 9). At 1292 F the weight gain was 0.00013 mg/cm²/hr (equivalent to a corrosion rate of 0.08 mpy). Phennah and Associates confirm that the coating is protective in this temperature range. (26)

Initially, at 1382 F the rate followed a similar pattern but is reported to show "break-away". If such a condition exists it is not clearly shown in Figure 9.

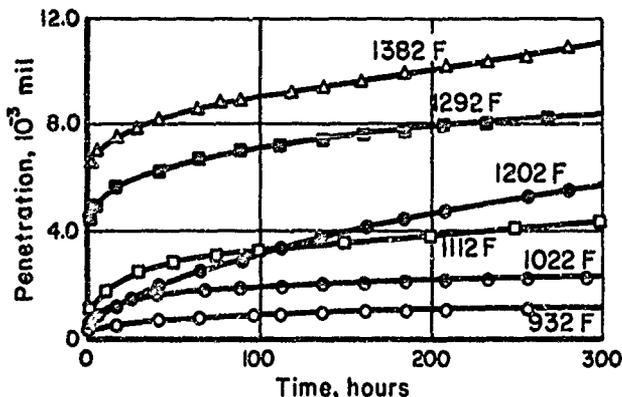


FIGURE 9. CALCULATED PENETRATION OF BERYLLIUM BASED ON OXIDATION IN CARBON DIOXIDE AT 10 CM PRESSURE (Reference 25)

In carbon monoxide, the coating is non-protective above 1022 F and the attack is greater than in carbon dioxide. Figure 10 illustrates this more rapid attack.

There is some reason to believe that the carbide inclusions in beryllium may be related to the corrosion resistance of the materials. Studies by Jepson and Associates using isotopically labelled carbon (C14) showed that the carbide inclusions are attacked in water vapor and in oxygen atmospheres at 1292 F, but that

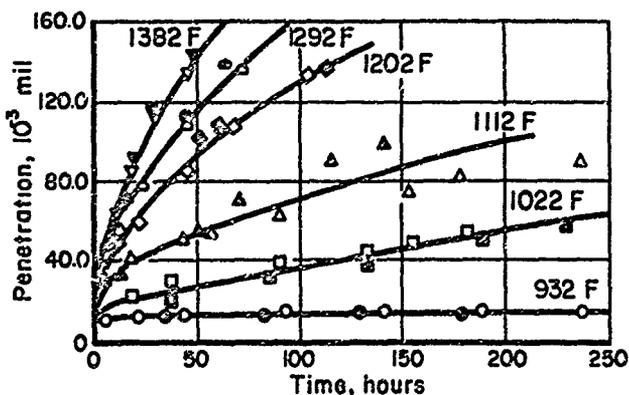


FIGURE 10. CALCULATED PENETRATION OF BERYLLIUM BASED ON OXIDATION IN CARBON MONOXIDE

The initial pressure was 10 cm and the runs terminated before the pressure had decreased to 5 cm. (Reference 25)

little attack occurs in carbon dioxide. (27) They found that rapid attack occurs preferentially along grain boundaries and, thus, may be related to carbides.

More recent autoradiographic studies by McCoy confirm that the reaction products with CO₂ are BeO and Be₂C. (28) He used specimens made by compaction and hot extrusion of high-purity Pechiney flake.

Moist Carbon Dioxide and Moist Carbon Monoxide. The oxidation of electrolytic flake beryllium was four times greater from the water-vapor component than from the carbon dioxide portion in the temperature range 932-1382 F according to Gregg and Associates. (29) The oxidation was protective up to 1112 F and nonprotective at 1202 F and beyond. The reaction with the water-vapor component contributed 97 percent of the total weight gain in the moist carbon monoxide system. The accelerating rates are associated with severe intergranular oxidation under blisters. (27)

A later paper by Jepson and Associates discusses further the action of moist carbon dioxide on Pechiney beryllium. (30) It was shown that at 1292 F numerous blisters develop on the oxide surface. The evidence suggests that cracking of these blisters exposes fresh surface and enhances rapid oxidation.

The importance of beryllium analysis and of the effect of method of fabrication on the corrosion resistance in carbon dioxide was discussed in some detail by Menzies. (31) He found that extruded materials in disk form had greater resistance to oxidation than sheet materials. Particular attention was given to reactions at 1112-1292 F.

The addition of at least 0.15 percent calcium to beryllium improves the corrosion resistance

of beryllium in CO_2 containing moisture, according to Raine and Robinson. (32) They showed, for example, that good resistance was furnished in CO_2 at 1292 F at 20.5 atmospheres whereas the upper temperature with unalloyed beryllium was 1112 F.

It was also reported by Scott and Ranzetta that the addition of 0.7 percent calcium reduced the extent of the intergranular oxidation of beryllium in moist CO_2 plus 2 percent CO at 1202 F and 300 psi. (33) It was also shown that calcium improved oxidation resistance in air.

Moist Helium. In helium containing 4 percent H_2O at 1112 F corrosion rates were similar to those found in carbon dioxide. (34)

Reactions With Combustion Gases. Workers at TRW Systems studied the reactions of beryllium with seven combustion gas species (O_2 , N_2 , H_2O , H_2 , NO , CO , and CO_2) at high temperatures. (22) Their primary interest was to determine the possibility of the release of airborne beryllium compounds at a launch-pad accident. They used QMV-grade beryllium containing 1.67 percent BeO . A comparison of the reactivity as measured by the amount of gas reacted is given in Figure 11 for all the above gases except water

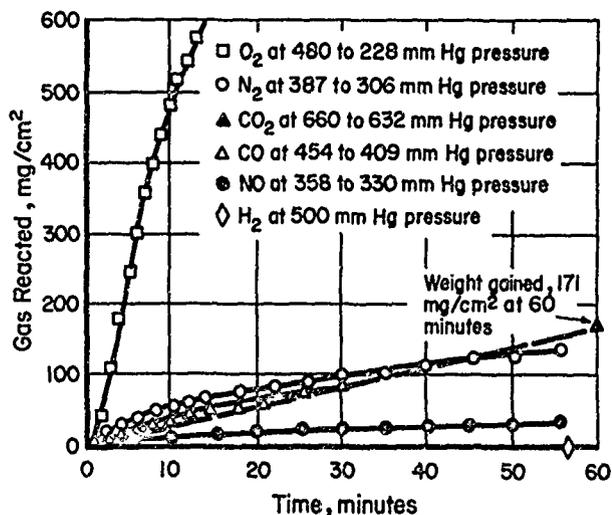


FIGURE 11. COMPARISON OF O_2 , N_2 , CO , H_2 , CO_2 , and NO reactions with Be at 2732 F (22)

vapor. Actually, they found that water vapor was more reactive than any of the other gases at temperatures below the beryllium melting point.

In general, beryllium reacts with nitrogen in much the same manner as with oxygen, except at a lower rate. The nitride film that is formed is insoluble in the metal and is protective and stable below 1600 F. (14)

As can be seen in Figure 11, no noticeable reaction was detected between beryllium and hydrogen at temperatures up to 2732 F.

Experiments at TRW indicated very little reaction of nitric oxide with beryllium below the melting point and only a small reaction at 2732 F (Figure 11).

Hydrogen Sulfide. Beryllium evinced no corrosion in a mixture of air with 50 percent H_2S and relative humidity of 50 percent at 68 F. (35) The specimens which were prepared by vacuum condensation of beryllium onto brass bases were exposed for 30 days.

Nitrogen Tetroxide and Aerozine 50. Studies in connection with the Apollo program indicated that beryllium was only slightly attacked by dry N_2O_4 . (36) When 5 percent by weight of water was added to the N_2O_4 , corrosion rates increased. Dry Aerozine-50 (50 percent N_2H_4 - 50 percent unsymmetrical dimethylhydrazine) did not attack beryllium, while material containing added water caused a slight attack.

A companion study showed that anodized beryllium is compatible with both dry and water-contaminated (5 percent) Aerozine-50. (37) The anodic coating was attacked by N_2O_4 .

High-strength forged beryllium specimens were exposed at ambient temperatures to nitrogen tetroxide and monomethylhydrazine for a period of 7 months. As reported by Soffa and Basl there was no evidence of corrosion, grain-boundary attack, or weight loss on the beryllium specimens. (38)

Halogens. From the review made by Cabanis and Williamson beryllium appears to be as resistant to fluorine as is nickel at temperatures below 600 F. (39) This behavior is related to the formation of a stable fluoride film. At temperatures in excess of 600 F nickel is more resistant.

Corrosion studies in liquid ClF_3 were carried out by Jackson using good-quality cross-rolled sheet that contained about 2.8 percent BeO . (40) After a 3-day exposure at temperatures ranging between 30 to 50 F, the corrosion rate was 0.37 mpy. In a second exposure of 17 days at 70-76 F, a rate of 0.17 mpy was obtained. It is believed that the higher rate in the short-term exposure was the result of HF produced from moisture contamination.

Organic Liquids

Solvents. Some organic cleaning solvents are detrimental to beryllium. Methyl alcohol in combination with water, Freon, or perchloroethylene reacts quickly. Methyl ethyl ketone in combination with Freon or water also reacts. (41, 14) Trichloroethylene and a number of other common solvents have been used to degrease beryllium, with no observed corrosive attack. A summary of the fluid reaction rates of various cleaning solutions with beryllium is given in Table 6 as taken from Steele. (41)

TABLE 6. FLUID REACTION RATE WITH
BERYLLIUM
(Reference 41)

Methyl alcohol and water (distilled)	Immediate chemical reaction
Methyl alcohol and Freon	Strong chemical reaction
Methyl alcohol and perchlorethylene	Chemical reaction
Methyl ethyl ketone and Freon	Chemical reaction in 3 minutes
Methyl ethyl ketone and water (distilled)	Reaction starts immediately
Perchlorethylene	No reaction
Freon (TF)	No reaction
Varsol	No reaction
Methyl alcohol	No reaction
Ethyl alcohol	No reaction
Acetone	No reaction
Water (distilled)	No reaction
Perchlorethylene and water (distilled)	No reaction
Freon and water (distilled)	No reaction
Acetone and water (distilled)	No reaction
Varsol and Freon	No reaction
Varsol and acetone	No reaction
Varsol and perchlorethylene	No reaction
Varsol and methyl alcohol	No reaction
Varsol and water (distilled)	No reaction
Methyl ethyl ketone	No reaction
Methyl ethyl ketone and Varsol	No reaction
Methyl ethyl ketone and acetone	No reaction
Methyl ethyl ketone and methyl alcohol	No reaction
Oakite No. 61	No reaction
Oakite No. 61 and acetone	No reaction
Oakite No. 61 and water (distilled)	No reaction

Terphenyls. Beryllium (Pechiney with 0.9 percent BeO) has good resistance to pure terphenyls according to Schleicher. (42) Exposures of 300 hours at 842 F produced slight weight gains from Terphenyl OM2, both dry (10 ppm water) and wet (500 ppm water). The specimens were discolored but not attacked.

Hydraulic Fluids. The corrosion resistance of QMV beryllium in hydraulic fluids, G. E. Versilube 81644, Oronite 8200, and MIL-L-7808C was good to temperatures in the range 450-650 F. (43)

Molten Materials

Sulfur. Beryllium has been exposed to molten sulfur at temperatures from 1100 F to 1500 F by AiResearch personnel. (44) Some shallow pitting was observed at 1300 F in 21 hours and heavy pitting was found at 1500 F in about 2 hours. When compared to materials such as stainless steels and superalloys, beryllium was superior.

Metals. The subject of corrosion by liquid metals up to about 5 to 10 years ago was reviewed by White and Burke (4) and Darwin and Buddery. (5) The following paragraphs present more recent reports of research in this area along with data in the above references.

The oxygen content of the system is of great importance in the corrosion of beryllium in liquid metals. Beryllium reacts with and reduces most oxides, nitrides, sulfides, and carbides. For example, the actual corrosion of beryllium by sodium or sodium potassium alloy (NaK) is very low, but the beryllium metal reduces any sodium oxide in the system to form BeO, which can accumulate as a nonadherent powder.

It should be mentioned, however, that according to Darwin a number of refractory oxides have given satisfactory service in containing molten beryllium. (5) Beryllia is favored as a crucible material.

Alkali Metals. Corrosion results for beryllium in molten lithium are summarized in DMIC Report 169 dated May 28, 1962. (45) It was pointed out that, based on a 6-day exposure test, beryllium exhibited very good resistance to lithium at 1100 F. (46) An intermetallic compound, NiBe, was formed on the surface of the beryllium due to the presence of nickel in the lithium.

Hoffman found 2 and 3 mils of intergranular attack on beryllium after 100 hours in lithium at 1500 F and 1832 F, respectively. (47)

Cunningham reported severe intergranular penetration of extruded beryllium at 1832 F. (48) The penetrations were about 4, 15, and 22 mils at 4, 40, and 400 hours of exposure, respectively.

Beryllium is very resistant to molten sodium (49) or sodium-potassium eutectic alloy (NaK), provided oxygen is excluded from the system. Beryllia (BeO) is formed when oxygen is present, and penetration rates of 12 to 60 mpy were reported in oxygen-containing NaK at 970 F. (5) The amount of oxygen present was not stated for the above work but must have been greater than 0.003 to 0.01 percent since Williams and Eyre report negligible attack at such oxygen levels at 932 F. (50)

Some success has been achieved in scavenging the oxygen in sodium systems by additions of calcium, which is quite soluble and is more reactive with oxygen than is beryllium. However, there are reports that calcium can be a source of nitrogen so that beryllium in the system becomes coated with a thin film of Be_3N_2 . (51,52) Since this film is hard and adherent, it may not be particularly harmful.

Excellent resistance is found in distilled sodium under an argon cover gas, whereas under a nitrogen blanket corrosion occurred because beryllium nitride was formed. (5) The rates, however, were only 3 mpy at 1100 F.

Beryllium is fairly resistant to attack by rubidium. Capsules made from 1/2-inch-diameter tubing of beryllium (98.36 percent Be-1.63BeO) were evaluated in rubidium at temperatures from 1000-2000 F in 1000-hr tests. (53) No corrosion was detected in either the liquid or vapor at temperatures up to 1400 F. At this temperature some surface roughening and scale formation was noted. On the basis of these studies it was concluded that beryllium would be adequate for holding rubidium at 1000 F. Further studies at 1400 F were recommended before qualifying beryllium at this higher temperature.

In another study, beryllium rod specimens (1.47 BeO) were exposed to rubidium in Type 316 stainless steel capsules at Battelle-Columbus for 500 hours at 900, 1200, and 1400 F. (54) Beryllium was mildly attacked by the rubidium at 900 and 1200 F, but marked surface pitting was found at 1400 F. The general depth of the pits was 0.6 mil.

Alkaline Earth Metals. Beryllium is quite resistant to magnesium and is unattacked after prolonged heating in boiling magnesium under an argon atmosphere. (5) It has also resisted molten magnesium alloys at temperatures up to 1112 F. (55)

According to Darwin, a beryllium container holding boiling calcium was soon coated with a layer of CaBe_{13} . (5) It was not stated as to whether this layer was protective to progressive penetration.

Zinc and Mercury. No attack was found from mercury at 600 F after 330 hours in the absence of air. (5) Since the zinc completely boiled away during an attempt to form a beryllium-zinc alloy by melting, it may be concluded that zinc does not form a compound with beryllium. (4)

Aluminum, Gallium, and Indium. Beryllium has poor resistance to molten aluminum as would be suggested by the solubility relationships. (5)

It is reported that the corrosion resistance to gallium is good to 932 F, limited at 1110 F, and poor at 1470 F. (5,55)

Indium and thallium are very likely less corrosive than gallium, according to Darwin. (5)

Antimony, Bismuth, and Lead. Straka reports that beryllium resisted molten antimony, lead, and bismuth at temperatures up to 1292 F in a 24-hour exposure. (55) In another study, a 5-hour exposure of beryllium to antimony at the above temperature showed no wetting of the beryllium and no apparent attack. (5)

Commercial-grade beryllium (99.3 percent Be) was found by Seifert and Lowe to be fairly resistant to molten bismuth under flow conditions. (56) Results obtained for specimens run in tilting capsules are summarized in Table 7. It

TABLE 7. TILTING CAPSULE TESTS OF AS-RECEIVED BERYLLIUM^(a) IN MOLTEN BISMUTH (REFERENCE 56)

Test	Specimen Preparation	Test Time, hours	Average Penetration, mpy		Remarks
			975 F	750 F	
1	As received	1000	0.153	0.313 ^(b)	No visible attack
2	As received	1000	0.504 ^(b)	0.322 ^(b)	No visible attack
3	As received	1000	Lost	0.990 ^(c)	No visible attack
4	As received	1000	0.683 ^(b)	0.045	No visible attack

(a) Test solution: Bi + 1150 ppm U, 350 ppm Mg, 175 ppm Zr.

(b) Small particle of specimen adhered to specimen holder upon removal.

(c) Part of specimen broke off during cleaning.

will be noted that corrosion rates are less than 1 mpy at 750 F and 975 F. Studies in a dynamic loop at 910 F at 4 and 8 feet per second indicated no significant effect attributable to velocity. The corrosion rates were close to 1 mpy.

A penetration of 3 to 5 mils was reported after 24 hours for beryllium in contact with bismuth at 1830 F. (4)

Exposure of beryllium at ORNL in a thermal loop containing molten lead at 1472 F in the hot section and at 932 F in the cooler section revealed a considerable accumulation of beryllium in the cold leg after 456 hours. (57) This mass-transfer effect indicates that dissolution of beryllium had occurred in the hot portions of the loop. It was noted that beryllium reduced SiO_2 from the walls of the loop during the operation.

At 1830 F the resistance to lead was considered to be only fair after 40 hours of exposure. (4)

Solid Materials

There is some information available concerning the interactions, such as diffusion,

between beryllium and solid materials in intimate contact with it.

Knapp and West measured the diffusion between beryllium and the metals iron, nickel, stainless steel, and uranium as well as uranium dioxide. (52) Specimens of beryllium in contact with the solid materials in evacuated capsules were heated to temperatures from 932 to 1472 F for times up to 224 days. The reaction-layer thickness (in microns) was measured and recorded as in Table 8.

TABLE 8. REACTION-RATE STUDIES OF BERYLLIUM WITH OTHER SOLID MATERIALS (REFERENCE 52)

Material	Time, days	Reaction-Layer Thickness, μ		
		932 F	1112 F	1292 F
Beryllium-iron	7	None observed	10	48
	14	8	10	80
	28	12	30	228
	56	24	40	240
	112	24	80	312
Beryllium-nickel	7	64	44	256
	14	120	60	350
	28	206	84	802
	56	210	124	1120
	112	180	280	1260
Beryllium-stainless steel	7	None observed	12	70
	14	14	35	90
	28	21	50	140
	56	30	66	184
	112	56	92	288
Beryllium-uranium	14	--	5	12
	28	4	10	--
	56	2	10	32
	112	4	14	40
	224	--	--	60
	254	--	20	--
Beryllium-UO ₂ (a)	14	1112 F None observed	1292 F 4	1472 F 20
	28	2	8	20
	56	2	10	80
	112	None observed	80	90
	224	36	110	140

(a) Also 7 days, 1832 F; 160 μ

Other studies showed that beryllium does not react or reacts only slightly with Ta, W, Cr plate, Cb, Mo, Ti, or Zr-0.5Mo in vacuum or CO₂ atmospheres with <10-ppm water at 1022

to 1112 F. (58) It does react with alumel, chromel, Cu, Ni, Nimonic 75, stainless steel, steel, U, and Zr.

Interlayers of Cr plate, Al₂O₃, ZrO₂, SiC, and WC prevented reaction between beryllium and stainless steel at 1112 F. Nitrided steel reacted with beryllium.

The above results must be compared with those of Baird and Associates who studied the compatibility of coupons of about 15 metals when clamped to coupons of beryllium for extended periods at elevated temperatures in highly evacuated capsules. (59) Results are summarized in Table 9. Tungsten showed no diffusion up to 1292 F. Metals that appeared to be completely compatible, at least up to temperatures of liquid formation, are aluminum, antimony, and magnesium.

Metal to metal layers of beryllium with chromium, titanium, uranium, and molybdenum were nonreactive or formed films less than 5 μ in thickness after exposure at 932 F for periods up to 1 month. No reaction was observed with beryllium sheet in contact with carbon. Molten beryllium does react with carbon. (5)

Incompatible metals at 932 F included copper, iron, nickel, columbium, tantalum, uranium, and zirconium.

As can be seen in Table 10, the presence of oxide films did not provide protection to most of the interlayers evaluated.

Vickers indicates some reactivity of beryllium with oxides at 1112 F in vacuum. (58) The reactivity of four oxides in increasing order is Al₂O₃, ZrO₂, SiO, and MgO.

Special Topics

Stress-Corrosion Cracking

The tendency for beryllium to fail by stress-corrosion cracking has not been studied under very many conditions to date. Experience with other metals and alloys would suggest that there are environments in which cracking will occur, but these are not defined at this time.

Most of the stress studies with beryllium have been conducted in salt water or seawater, and these investigations have not indicated susceptibility to stress-corrosion cracking. A summary of results is given in the following paragraphs.

No failures were found with specimens cut from QMV block and from QMV hot-rolled sheet at Lockheed. (60) Both bare and anodized specimens were stressed to 90 percent of the yield

TABLE 9. REACTION OF BERYLLIUM WITH VARIOUS MATERIALS (Reference 59)

Material	Temperature, F	Time, days	Thickness of Reaction Product	Remarks
Aluminum	1112	8.5	No reaction	Compatible
Antimony	1292	5 hr	No reaction	Compatible
Carbon	932	18.5	No reaction	Compatible
	1112	8.5	No reaction	Compatible
Chromium	932	28	No reaction	Compatible
	1112	14	No reaction	Compatible
Copper	932	29	18 μ	Incompatible
Iron	932	29	8 μ	Incompatible
Magnesium	932	8.5	No reaction	Compatible
Nickel	932	31	40 μ	Incompatible
	1112	30	170 μ	Incompatible
Columbium	932	31	5 μ (irregular)	Incompatible
Tantalum	932	31	8 μ (irregular)	Incompatible
Titanium	932	31	No reaction	Compatible
	1112	30	3 μ	Incompatible
Uranium	932	28	4 μ (irregular)	Incompatible
Uranium with cast beryllium	1112	28	10 μ	Incompatible
Uranium	932	28	No reaction	Compatible (?)
	932	56	Very occasional 2 μ spots	Compatible (?) Compatible (?)
	1112	14	5 μ	Incompatible
	1112	56	6 μ with 10 μ spots	Incompatible
	1292	14	12 μ	Incompatible
Uranium/UC Cermet 1	1112	14	3 μ	Incompatible
0.251% carbon	1292	14	33 μ	Incompatible
Uranium/UC Cermet 2	1112	14	6 μ	Incompatible
0.5% carbon	1292	14	33 μ	Incompatible
Uranium/UC Cermet 3	1292	14	16 μ	Incompatible
1.0% carbon				
UC Cermet 4	1112	14	3 μ (irregular)	Incompatible
4.71% carbon	1292	14	43 μ	Incompatible
Zirconium	932	31	30 μ	Incompatible
Zircaloy	932	29	34 μ	Incompatible

strength and exposed to 3 percent salt spray at 90 percent relative humidity and 95 F for 100 hours. The tensile strength for the block material was defined as 36,000 psi and for the sheet material as 69,000 psi. The maximum depth of corrosive attack was 2 mils on the sheet specimens and 3 mils on the block coupons.

The same investigators exposed bare specimens stressed to 90 percent of the yield strength to various solutions chosen because they induce cracking in other metals. The solutions and results are shown in Table 11. No stress-corrosion cracking was detected. The results are difficult to interpret because the electrode potentials were varied by impressing a potential between the specimen and a graphite electrode. Since the open-circuit electrode potentials are not defined, it is not known if the specimens were moved in the anodic or cathodic direction. The true stress-corrosion effect could thus have been masked by the technique used. The results in the table are of value, however,

in furnishing information as to the general corrosive attack of various solutions on beryllium. It will be noted that many of them induced pitting rapidly.

Logan and Hessing exposed stressed, extruded, and pressed and sintered beryllium specimens to a circulating 0.002 to 0.006 molar hydrogen peroxide solution at 185 F to 193 F. (61) The pH of the water was about 6.3. These specimens were stressed to between 90 and 95 percent of their yield strength and were exposed for at least 785 hours. There was no evidence of stress-corrosion cracking. Some pitting was reported.

Corrosion studies made by L. P. Bornwasser, as described by English, included the exposure of stressed beryllium to a static aqueous, 0.005 molar solution of hydrogen peroxide at 194 to 203 F. (62) There was no evidence of intergranular attack.

TABLE 10. REACTION OF BERYLLIUM WITH VARIOUS MATERIALS IN THE PRESENCE OF OXIDE OR OTHER INTERLAYERS (Reference 59)

Material	Temperature, F	Time, days	Thickness of Reaction Product	Remarks
Beryllium-iron (beryllium oxidized 2 hr in oxygen at 1472 F)	1112	14	6 μ	Incompatible
	1292	14	10 μ	Incompatible
Beryllium-18/8 stainless steel (beryllium oxidized as in beryllium-iron)	1112	14	12 μ	Incompatible
	1292	14	70 μ	Incompatible
Beryllium-nickel (beryllium oxidized as in beryllium-iron)	1112	14	24 μ	Incompatible
	1292	14	130 μ	Incompatible
Beryllium-uranium (beryllium oxidized as in beryllium-iron)	932	28	No reaction	Compatible
	1112	14	2 μ	Incompatible
	1292	14	6 μ	Incompatible
Beryllium-uranium (natural oxide film on beryllium)	1112	28	8 μ	Incompatible
Beryllium-uranium (natural oxide film on uranium)	1112	28	8 μ	Incompatible
Beryllium-uranium (uranium oxidized for 2-1/2 hr in wet argon)	1112	14	Occasional large spots 6 to 12 μ thick	Incompatible
Beryllium-uranium (uranium oxidized for 1 hr at 1202 F in poor vacuum)	932	14	None	Compatible
	1112	14	Traces	Incompatible
	1292	14	14 μ	Incompatible
Beryllium (oxidized as in beryllium-iron and uranium) (oxidized in wet argon)	1112	14	Occasional spot 2 μ thick	Incompatible
	1292	14	16 μ	Incompatible
Beryllium-uranium (in presence of Aquadag layer)	1112	14	3 to 4 μ	Incompatible
	1292	14	20 to 30 μ	Incompatible

No failure was observed for stressed specimens (60 percent of yield) after a 30-day exposure at room temperature or at 120 F in 85 percent relative-humidity atmosphere. (86) Two specimens, one etched and the other unetched before anodizing, were evaluated.

An extensive study of stress-corrosion cracking was recently reported by Gilpin and Mackay using forged rods of beryllium (about 3 percent oxide) machined into tensile specimens. (7) The specimens stressed to 80 percent of the yield strength (about 85,000 psi) were exposed to a 5 percent NaCl solution for 10 minutes. The solution was then drained for 50 minutes while the specimens dried. The cycle was repeated to 500 hours. Results for bare and coated specimens are summarized in Table 12. (Coating procedures are discussed in another section of this report.) Pitting occurred on most of the specimens and the bare pieces

failed in about 50 hours because of this pitting rather than because of stress-corrosion cracking. The coated specimens survived 500 hours.

The same investigators held bare, anodized, SermeTel W coated and aluminized tensile rods of beryllium at 80 percent of the yield strength for 500 hours at 200, 400, and 600 F after the specimens were coated with a thin layer of salt. No chemical attack due to the presence of salt was observed on any specimen and none failed during the 500-hr exposure.

At Battelle-Columbus seven specimens each of beryllium and of 62 Be-38 Al alloy were evaluated for susceptibility to stress-corrosion cracking by immersion in 3-1/2 percent sodium chloride at room temperature. (63) Four-point loading was used and specimens were stressed to 80 percent of the tensile yield strength. No specimens had cracked after 1000 hours of exposure. The beryllium specimens were badly pitted, however.

TABLE 11. RESULTS OF EXPOSURE OF STRESSED BERYLLIUM COUPONS TO VARIOUS CORROSIVES (Reference 60)

Stress level 90 percent of the tensile yield strength

Solution Composition	pH ^(a)	Electrode Potential, $v^{(b)}$	Cracking	Remarks
20 g/l potassium chromate 35 g/l sodium chloride	8.4	0.75	No	General attack immediately Pitting in 120 hours
20 g/l potassium chromate 35 g/l sodium chloride	2.0	0.75	No	General attack accelerated Pitting in 48 hours
20 g/l potassium chromate 35 g/l sodium chloride	10.5	0.75	No	Rate of general attack decreased Less than 1 cm ² in 24 hours
20 g/l potassium chromate 35 g/l sodium chloride	8.4	1.26	No	Immediate general attack and pitting
20 g/l potassium chromate 35 g/l sodium chloride	8.4	0.36	No	Immediate general attack and pitting
57 g/l sodium chloride 3 g/l hydrogen peroxide	5.3	0.73	No	Immediate general surface attack Deep pits in 1 week
57 g/l sodium chloride 3 g/l hydrogen peroxide	5.3	1.16	No	General surface attack accelerated
57 g/l sodium chloride 3 g/l hydrogen peroxide	5.3	0.51	No	Lower rate of attack No pitting
53 g/l sodium chloride 50 g/l sodium chromate	2.0	0.73	No	Immediate general surface attack Pitting after 200 hours
53 g/l sodium chloride 50 g/l sodium chromate	11.0	0.73	No	No corrosion in 1 month
53 g/l sodium chloride 50 g/l sodium chromate	5.6	0.73	No	Slight corrosion after 1 month Two 1-mm ² areas
53 g/l sodium chloride 50 g/l sodium chromate	5.6	1.11	No	No corrosion
53 g/l sodium chloride 50 g/l sodium chromate	5.6	0.36	No	No corrosion
36 g/l chromic acid 3 g/l sodium chloride 30 g/l potassium dichromate	1.0	--	No	Severe pitting immediately Any cracking would be masked
10 g/l potassium fluoride	5.5	0.81	No	Immediate general surface attack
10 g/l potassium fluoride	8.0	0.81	No	Immediate general surface attack
10 g/l potassium fluoride	11.0	0.81	No	Rate of general attack decreased Slight attack

TABLE 11 (CONTINUED)

Solution Composition	pH ^(a)	Electrode Potential, $v^{(b)}$	Cracking	Remarks
10 g/l potassium fluoride	8.0	0.16	No	No corrosion in 24 hours
10 g/l potassium fluoride	8.0	0.51	No	Immediate general attack
1% sulfuric acid	1.0	--	No	General surface attack which subsided after 24 hours
100 g/l ferric chloride	2.0	--	No	Immediate reaction - severe general corrosion Iron deposited on beryllium
100 g/l cupric sulfate	4.0	--	No	Immediate reaction - general corrosion Copper deposited on beryllium
100 g/l magnesium chloride	4.3	0.86	No	Immediate general corrosion
100 g/l magnesium chloride	4.3	0.56	No	General attack accelerated
100 g/l magnesium chloride	4.3	1.16	No	No corrosion in 24 hours
100 g/l sodium metasilicate	11.5	-0.4	No	No corrosion in 7 days
100 g/l sodium metasilicate	11.5	0.46	No	No corrosion in 7 days
100 g/l sodium metasilicate	11.5	-0.19	No	No corrosion in 7 days

(a) pH adjusted by addition of acid or base without introduction of different ions.

(b) Steady-state electrode potential referenced against a saturated calomel half cell.

TABLE 12. RESULTS OF ALTERNATE IMMERSION TESTS ON STRESSED SPECIMENS IN 5 PERCENT NaCl (Reference 7)

Specimen	Coating	Time in Test, hrs	Remarks
A-1	Bare	75	Failed during test by corrosion pitting
19-4	Bare	53	Failed during test by corrosion pitting
23-3	Bare	57	Failed during test by corrosion pitting
13-5	Anodize	500	Pitted but no pallure
13-5	Anodize	500	Pitted but no failure
5-3	SermeTel W	500	Thread failure
6-4	SermeTel W	500	Pitted but no failure

According to Lindgren and Associates, stressed beryllium exposed to 3 percent salt spray and solutions of potassium chromate, sodium chloride, potassium fluoride, or magnesium chloride for 100 hours showed no evidence of stress-corrosion cracking. (64) Both anodized and bare specimens were evaluated. Some minor corrosion was noted. Pitting was experienced in dilute hydrogen peroxide solutions.

The only indications of harmful effects from stress on beryllium corrosion were reported by Prochko and Associates. (9) They report that both bare pickled beryllium and anodized beryllium failed prematurely at applied stresses well

below the yield strength when exposed to seawater at ambient temperatures (59 F).

The average time to failure for pickled beryllium was 490 hours at 20,000 psi and 305 hours at 30,000 psi. The yield strength of this material was about 55,000 psi. The average time to failure of anodized specimens was about 360 hours for both stresses.

Studies made by the same investigators in synthetic seawater showed that the average time to failure decreased from about 2350 to 40 hours as the applied stress was increased from 1220 to 40,000 psi, respectively (Figure 12). (10) The specimens were prepared from 0.060-inch-thick commercial-purity beryllium (98.3 percent Be containing 1.63 percent BeO) sheet material. The sheet was cross rolled, surface ground, and flash pickled. The yield strength was about 64,000 psi. The specimens (run in quadruplicate) were totally immersed in the solution, which was changed every 48 hours. Failure in all cases was in a direction normal to the applied stress and was transgranular.

It was concluded that the failure was not due to stress-corrosion cracking but rather to stress-accelerated corrosion and was closely associated with random pitting attack. There was no greater incidence in the pit density observed but the effect rather was that certain pits or possibly one pit only became active and penetrated

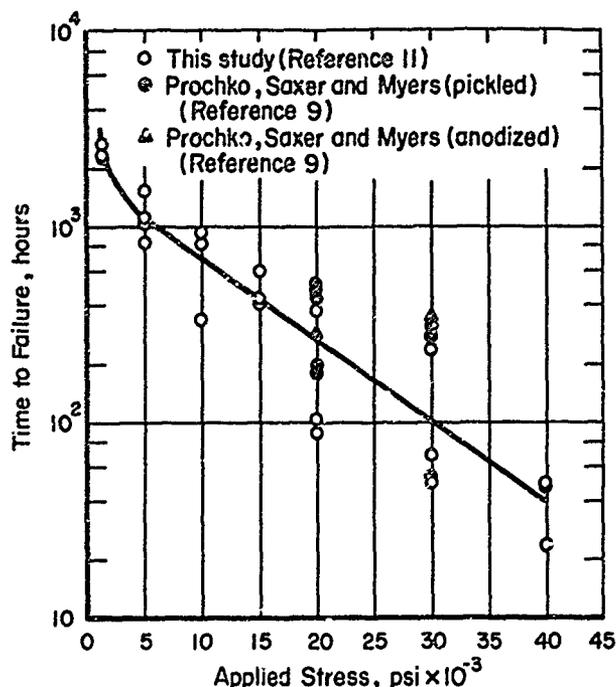


FIGURE 12. EFFECT OF APPLIED STRESS ON THE TIME TO FAILURE FOR STRESSED, PICKLED BERYLLIUM SHEET MATERIAL TOTALLY IMMERSSED IN SYNTHETIC SEAWATER AT 77 F

the metal very rapidly. (65) The final failure was attributed to one or both of the following:

- (1) Increased stress concentration at pits.
- (2) Decreased cross-sectional area.

The fractured surface was bright over one region and dark over the area where the localized attack had occurred.

More recent results from the same laboratory revealed that small cathodic current densities eliminated stress-accelerated corrosion and that anodic currents reduced the time to failure (Figure 13). (65) Specimens were stressed at 30,000 psi in aerated synthetic seawater. The higher the anodic current density, the shorter the time to failure. It should be noted that cathodic tests were not run beyond 200 hours. The investigators concluded that the stress-corrosion mechanism is electromechanical and is not associated with embrittlement by hydrogen.

Harlow and Glessner studied the effect of stress during exposure of Lockalloy (62Be-38Al) to N_2O_4 containing 0.09 percent O_2 at 120 F. (66) Three specimens were stressed by four-point loading at 50 percent of the ultimate (about 50,000 psi transverse and about 54,500 psi longitudinal). No failure occurred during a 30-day exposure. A slight permanent set was observed in the specimens after the test. An average weight loss of 0.001 g resulted from the

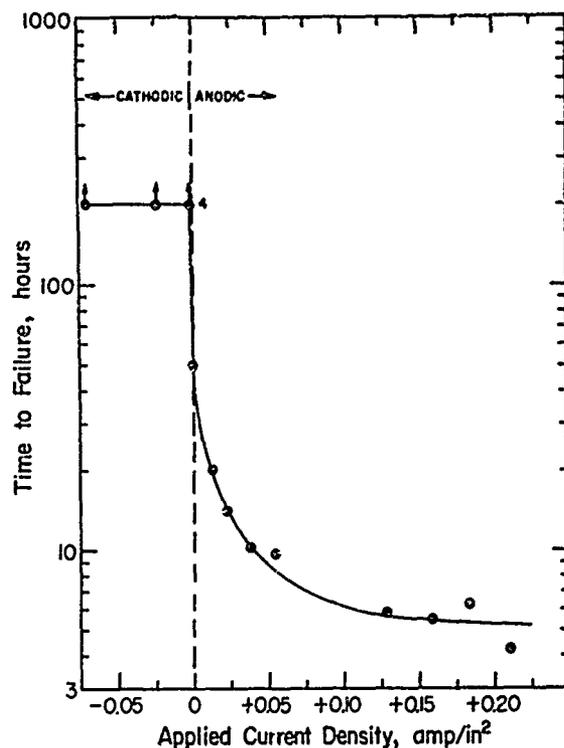


FIGURE 13. EFFECT OF IMPRESSED CURRENTS ON STRESS FAILURE OF BERYLLIUM (Reference 65)

exposure of the 0.5 x 3 x 0.032-inch specimens. The specimens weighed about 1.2 gram.

Galvanic Effects

Beryllium is an electropositive (active) metal and would be expected to corrode in many galvanic cells.

Accelerated corrosion of beryllium has been reported for beryllium coupled to aluminum and its alloys or to Type 347 stainless steel. White and Burke summarized results from the Oak Ridge National Laboratory which showed enhanced pitting at 185 F of beryllium coupled to pure aluminum and Type 356 aluminum in water containing enough H_2O_2 to adjust the pH to about 6. (4) Pits 4 to 6 mils deep were produced in about 60 days. Similar results were obtained with Type 347 stainless steel. Pits less than 5 mils deep and ranging from a density of 5 to 20 pits per square centimeter were encountered in the beryllium. In general, corrosion rates for beryllium were raised about five times by coupling to aluminum or stainless steel.

Protective Coatings and Surface Treatments

The status of protective coatings for beryllium was summarized several years ago by Beach and somewhat more recently by Stonehouse. (67) (2)

Coatings have been applied by anodizing, pack cementation, enameling, chemical conversion, and coating with a beryllium slurry followed by fusion, electroplating, or electroless plating (Van Thyne).⁽⁶⁸⁾

Pretreatments

The importance of surface preparation, cleanliness, and pretreatment on the corrosion resistance of beryllium is quite great.^(2,18)

Machining procedures must be considered because microcracks can be produced. The cracks are potential trouble spots from the corrosion standpoint since contaminants can readily be retained in them. Etchants can be used to remove the outer surface and eliminate the cracks. Typical solutions used for such a purpose are given in Table 13. Etchants for other purposes are also included.

It should be emphasized that cleaning a fabricated part followed by adequate rinsing and drying will improve the corrosion resistance. Contact with tap water or water containing chlorides and sulfates should be avoided.

A fairly extensive discussion of surface-treatment techniques developed for use in the fabrication of beryllium aerospace vehicle structures was presented by Williams and Ingels.⁽⁶⁹⁾ They conclude that surfaces should be wiped with lint-free cloth or paper tissue wet with methyl ethyl ketone. This treatment removes lubricants, layout dyes, and other superficial contaminants. Oxide films and deeply

etched "fingerprints" may be removed by wet grinding (180-mesh aluminum oxide) followed by light etching. Etchants suggested are sulfuric acid, nitric-hydrofluoric acid, or ammonium bifluoride solutions. Details of handling, bonding, and plating are also included in the above report.

A typical surface preparation used for preparing machined round specimens from forged rods at Astropower was to take a series of finishing cuts such as 0.020 inch, 0.010 inch, 0.005 inch, 0.003 inch, and 0.001 inch.⁽⁷⁾ After machining, 0.001 inch was removed by polishing longitudinally at 1500 rpm with 240-, 400-, and 600-grit papers. As a final operation 0.002 inch was removed by etching in 30 percent HNO₃, 0.5 percent HF in deionized water. Etching was conducted at 75 F, which produced an etch rate of about 0.001 inch in 10 minutes. Rinsing was done in deionized running water for a minimum of 2 minutes at ambient temperature. Specimens were blown dry with clean air.

Chemical-Conversion Coatings

Useful coatings have been produced on beryllium by chemical reactions between the metal surface and a properly formulated solution.

Chromate Coatings. An earlier section of this report indicated rapid oxidation of beryllium in air at temperatures near 1652 F. Pearlstein and Associates found that chromate conversion coatings applied to beryllium prevented oxidation for 24 hours at 1652 F in air containing water vapor.⁽⁷⁰⁾ The coating was produced by 30-minute immersion at 77 F in a proprietary

TABLE 13. COMMON ETCHANTS FOR BERYLLIUM (Reference 18)

Nomenclature	Composition	Characteristic Finish	Application
Chemical polish	26.5 ml con. H ₂ SO ₄ 450 ml con. H ₃ PO ₄ 53 g CrO ₃ Use from 110 to 250 F	Bright polish which remains for long times. Orange-peel texture may be developed. Very fast removal rate.	Standard etch - Tensile bars and general pickling of surface.
HF-HNO ₃	20 ml HF 500 ml HNO ₃ 480 ml H ₂ O Generally used near room temperature.	Smooth matte finish. Moderate removal rate.	Use to clean metal prior to welding or electroplating.
Ammonium bifluoride	5 - 10 g NH ₄ F·HF 100 ml H ₂ O	Smooth matte finish. Moderate removal rate.	General etching.
Electropolish	100 ml H ₃ PO ₄ 30 ml H ₂ SO ₄ 30 ml glycerol 30 ml absolute ethanol	Bright polished surface. Attack may not be uniform, resulting in pits.	Used principally for metallography.

chromating solution normally used for aluminum (U. S. Patent 2796371). The specimens were 1.3 cm in diameter by 1.3 cm long. The metal was hot pressed, extruded, machined, and then coated. Figure 14 shows the details of the oxidation results and includes a comparison of bare and chromated beryllium. It will be noted, however, that the oxidation of chromated beryllium is accelerating after about 50 hours of exposure.

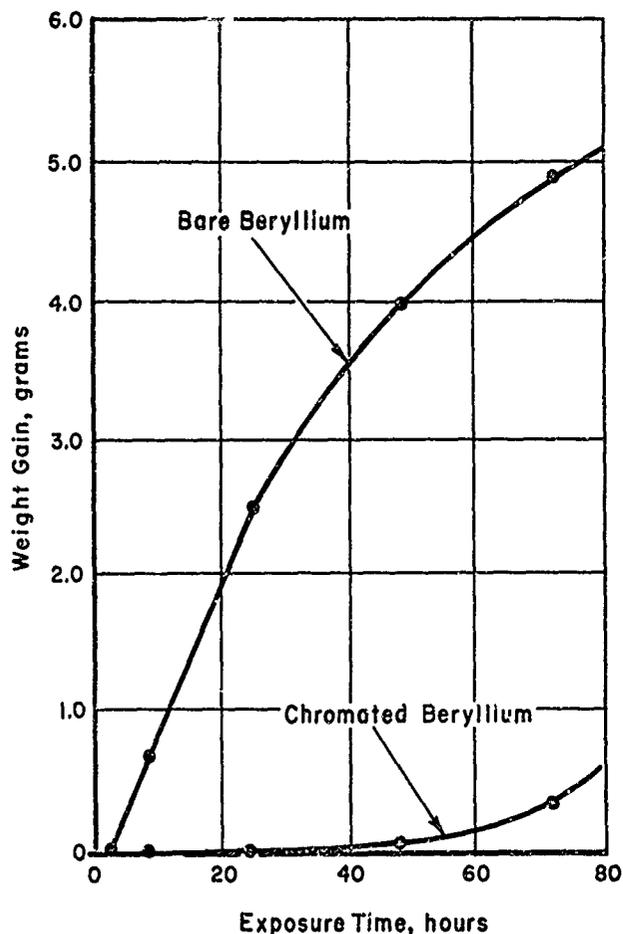


FIGURE 14. OXIDATION OF BARE AND CHROMATED BERYLLIUM IN MOIST AIR AT 1652 F (Reference 70)

Fluoride Coatings. A recent report by O'Donnell indicates that a fluoride film on beryllium will provide corrosion protection. (71) The film is produced by treating beryllium in fluorine above 970 F. A rhombic tridymite type structure is produced that has a glassy appearance and is insoluble in water in contrast to other modifications which are extremely soluble. Figure 15 shows the improved corrosion resistance for specimens (sample size not given) coated in fluorine at 1150 F and 200 torr. These specimens along with uncoated pieces were exposed to distilled water and to tap water for extended periods. It is pointed out that the fluorinated sample in distilled water remained essentially unchanged for about 3000 hours whereas the bare piece gained considerable weight.

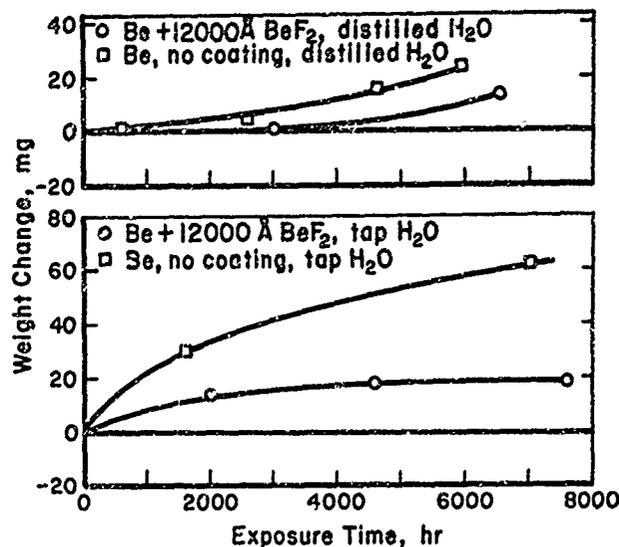


FIGURE 15. STATIC TEST WEIGHT CHANGE (Reference 71)

Metallic Coatings

Metallic coatings are applied to beryllium to facilitate joining by soldering or by pressure bonding at moderately low temperatures. Such coatings also are used to improve the wear resistance and corrosion resistance of beryllium. A fairly detailed report on procedures for coating beryllium was prepared several years ago by Beach as DMIC Memorandum 197. (67) The following paragraphs on metallic coatings contain information from that memorandum and it should be noted that much of the content comes from an earlier paper. (72)

Since the majority of applications for beryllium have involved temperatures up to 1500 F, the metallurgy of the coated, composite system is important in the design of beryllium parts. Interdiffusion of a multimetal system will result in continually changing interfacial layers. Thus, the ultimate operational characteristics of the composite system will be affected by the properties of the various alloys that are formed.

Nickel, iron, chromium, and silver offer promise as preferred metallic coatings on beryllium for elevated-temperature applications. Nickel-coated beryllium shows no undesirable interfacial alloying after 30 days at 600 F. However, the diffusion between the nickel and beryllium that occurs in 30 days at 932 F results in brittle, low-strength, interfacial alloy layers. Iron-coated beryllium shows alloying characteristics similar to those of nickel-coated beryllium but with slightly lower rates of diffusion.

Electrodeposited Coatings. Adherent metallic deposits can be obtained on beryllium if careful attention is given to the procedures used. Greases and oils are best removed by organic-solvent degreasing (vapor or contact). Residual

dirt is removed by cathodic cleaning in alkaline detergent solutions. Proprietary cleaning solutions containing caustic, carbonate, and/or wetting agent, such as those devised for aluminum, copper, magnesium, etc., can be used satisfactorily.

Beach points out that, if needed, the surface can be descaled by pickling in a hydrofluoric-nitric acid solution (2 vol percent of 48 percent HF, 50 vol percent of 70 percent HNO₃, and 48 vol percent of water at room temperature).

After precleaning and water rinsing, the beryllium is often prepared for electroplating by use of a zinc-immersion coating. (67,72) The clean beryllium part is immersed in the following solution at 185 ±5 F for about 5 minutes to produce the thin, uniform zinc displacement film on the surface:

Sodium tetraprophosphate - Na₄P₂O₇ -
120 g/l

Zinc sulfate - ZnSO₄ · 7H₂O - 40 g/l

Sodium fluoride - NaF - 7.5 g/l

Potassium carbonate - K₂CO₃ - 5 g/l

pH 7.5-8.0 with sulfuric and/or phosphoric acid.

The adherent zinc film is a basis for subsequent electroplating with copper and/or other metals from solutions designed for plating on zinc. An alternative procedure for plating on beryllium is as follows. (67,73)

(a) Anodic pickle

Phosphoric acid (85% H₃PO₄), 10%
(by volume)

Hydrochloric acid (38% HCl), 2% (by
volume)

Temperature, 80 ±10 F

Current density, 15 ±5 amp/sq ft

Time, 1 min

(b) Chemical pickle (without rinsing)

Concentrated nitric acid (70% HNO₃)

Temperature, 80 ±10 F

Time, 2 min

(c) Water rinse

(d) Acid dip

Ammonium sulfate - NH₄(SO₄)₂, 100 g/l

Sulfuric acid - H₂SO₄, 10 g/l

Temperature, 80 ±10 F

Time, 1/2 to 1 min

(e) Water rinse

(f) Electroplate

Metals that have been electroplated on beryllium include copper, tin, silver, chromium, aluminum, iron, nickel, and zinc.

Another direct-plating method has been described by Missel as follows: (73)

(a) Abrasive clean

Wet 400-grit emery paper

(b) Water rinse

(c) Anodic clean

5 minutes with current density of 50
amp/sq ft in a mild brass-type cleaner
at 130 F

(d) Water rinse

(e) Acid etch

Nitric acid (70% HNO₃) - 5 vol percent
Hydrofluoric acid (48% HF) - 1 vol
percent
Water - 94 vol percent at room temper-
ature, 30-second immersion

(f) Water rinse

(g) Acid activate

Sulfuric acid - 3.6N H₂SO₄ at room
temperature; 30 to 60-second immer-
sion

(h) Water rinse

(i) Nickel plate

Proprietary all-sulfamate bath pH
3.0 to 3.5
Temperature, 130 F
Current density, 50 amp/sq ft

(j) Water rinse and dry

It was reported that coatings 7 mils thick produced on beryllium by the above procedure have withstood a solar-furnace test in which the underlying beryllium could be heated to its melting point (2341 F) in about 9 seconds.

Electroless Coatings.

Electroless Nickel.⁽⁶⁷⁾ Electroless nickel on beryllium is being considered for various applications because it is a hard and wear-resistant coating.^(74, 75)

The coating, a nickel-phosphorus alloy containing 6 to 8 percent phosphorus in solid solution, is nonmagnetic until heated at 750 F and above. The alloy has a coefficient of thermal expansion of 7.2×10^{-6} in./in./F, which compares favorably with that of beryllium, 6.3×10^{-6} in./in./F.

Camera mirrors are electroless-nickel coated, polished, and flash-aluminum coated for aerospace needs. The electroless-nickel coating, "Kanigen",* polishes like glass, and the thin, vacuum-deposited aluminum provides the needed tarnish resistance.⁽⁷⁶⁾

Pretreatment of beryllium for electroless-nickel plating involves precleaning and application of an immersion zinc film.⁽⁷⁷⁾ Kanigen plating is accomplished without any intermediate coating.⁽⁷⁶⁾ Reported data on electroless-nickel-coated beryllium are very limited.

According to Gilpin electroless nickel did not protect beryllium in a 5 percent salt fog spray at 100 F for 30 days.⁽⁷⁾

Electroless Platinum. Platinum-black coatings on beryllium were investigated by Missel and Greear to consistently provide a reliable high, total, infrared emittance surface (>0.8) for large parts.⁽⁷⁸⁾ The following processing steps were developed and adapted to the coating of hemispherical parts of beryllium using spray-coating techniques:

(a) Precleaning

1. Abrade with wet emery paper or cloth of 180 mesh or finer.
2. Alkaline clean and water rinse.

(b) Activation

1. Acid treat with 3.6N H₂SO₄ for 2 to 3 minutes and water rinse.

2. Zincate treat with zinc chloride solution for 1/2 to 1 minute and water rinse.

(c) Black platinizing

1. Treat with chloroplatinic acid solution for about 2 minutes and water rinse.
2. Alcohol rinse and dry.

All solutions are at ambient temperature. Drying after Steps (a2), (b1), or (b2) apparently is not detrimental. The zincate solution (b2) contains 100 g/l of ZnCl₂ in water adjusted to a pH of 4.9 ± 0.1 with acetic acid. The platinizing solution contains 10 g/l of chloroplatinic acid in water.

Miscellaneous Coatings

A beryllium-silicon fused metallic coating has been developed for high-temperature oxidation resistance.⁽⁶⁸⁾ The process includes the application of a lacquer-suspended slurry (35 to 70 weight percent silicon) followed by fusing at temperatures in the range 2100 to 2150 F. Coatings containing 50 percent silicon were still protective after 1300 hour at 1550 F (+6 F dew point), whereas coatings anodized in 20 and 40 percent chromic acid failed after 1204 hours.

SermeTel (Type W) is a ceramically bonded aluminum coating manufactured by Teleflex, Inc., used by Gilpin and MacKay.⁽⁷⁾ The specimens were lightly dry grit blasted with 200-mesh SiO₂ and cleaned with a dry-air blast. The SermeTel W was immediately applied with an air brush. After the specimen was coated, it was dried at 175 F for 15 minutes and cured at 650 F for 15 minutes. Two separate coatings giving a total thickness of 1.5 mils were applied. Specimens covered with this coating along with some coated with vacuum-deposited aluminum were alternately exposed to 5 percent salt fog at 100 F for 16 hours and temperatures ranging up to 800 F for 8 hours.

Only very slight corrosion could be detected by visual observation and by weight-gain measurements on all of the SermeTel W coated beryllium. The small weight increases were probably the result of oxidation of the SermeTel W coating. At 800 F small pits were detected at approximately the sixth cycle. The pits increased in size, but not in number, during subsequent cycles.

Vacuum-deposited aluminum coatings were blistered rapidly at 200, 400, and 600 F. Most of the aluminum disappeared during the first few cycles.

*Trade Name of General American Transportation Corporation.

Anodized Coatings

Anodic coatings have been shown to improve the corrosion resistance and air-oxidation resistance of beryllium. The coatings are produced by treating the metal in aqueous solutions by anodizing with ac or dc. The bath compositions in Table 14 were used in studies reported

TABLE 14. TYPICAL ANODIZING BATHS
(Reference 68)

Bath	Composition	Temperature, F
1	5,20,40 percent CrO ₃	41,120
2	10 percent Na ₂ Cr ₂ O ₇	75
3	10 percent Na ₂ CrO ₄	75
4	5N HNO ₃	95
5	10 percent NaOH	105
6	20 percent CrO ₃ plus 5 percent Al ₂ K ₂ (SO ₄) ₄ ·24H ₂ O	75
7	20 percent CrO ₃ plus 5 percent Al ₂ (SO ₄) ₃ ·18H ₂ O	75
8	20 percent CrO ₃ plus 20 percent Na ₂ Cr ₂ O ₇	75
9	10 percent CrO ₃ plus 10 percent Na ₂ CrO ₄	75
10	10 percent CrO ₃ plus 10 percent Na ₂ Cr ₂ O ₇	75
11	10 percent HNO ₃ plus 200 grams per liter CrO ₃	--

by Van Thyne⁽⁶⁸⁾ and Kerr.⁽⁷⁹⁾ Most of this anodizing was done with dc.

Packer surveyed many procedures and concluded that more uniform, adherent coatings were obtained using either of the following:⁽⁶⁰⁾

- (1) Solution of 50 percent HNO₃ at 20 amp/ft², 5 minutes
- (2) Solution of 7.5 percent NaOH at 10 amp/ft², 20 minutes.

A fairly extensive study of the polarization response of beryllium in various electrolytes was reported by Levy.⁽⁸⁰⁾ Chromates and phosphates, particularly in neutral pH solution, induced considerable anodic polarization. Beryllium oxide coatings are anodically formed with chromate, nitrate, aluminate, and hydroxide solutions. The beryllium was attacked anodically in fluoride, chloride, chlorate, and sulfate solutions. Cathodic polarization was less pronounced than anodic. Hydrogen-evolution characteristics were similar in all solutions.

Chromic acid anodizing of beryllium produces an adherent, glossy-black film of BeO about 0.1 mil in thickness.^(81,82) Various

processes are described by Stonehouse and co-workers.^(2,18,83) The anodic coatings (nitric-chromic acid solutions) increased in thickness linearly with applied voltage.⁽⁷⁹⁾ The coating does not form a dielectric film. Other studies showed that the anodized layers are crystalline and grew as platelets with a mean diameter of about 60 Å and a mean thickness of about 20 Å.⁽⁸⁴⁾

Coating Uses. Anodic coatings produced at Brush protected beryllium completely in a humidity-cabinet test for over 100 cycles (2400 hours).⁽²⁾ No pitting or attack of any nature was found on similar specimens exposed to deionized water or tap water for 3 months at 100 F. Anodized beryllium showed no failure in standard ASTM salt-spray tests for 2000 hours and possibly longer.

The same investigators found that anodized coatings protected beryllium from oxidation at high temperatures.^(2,18) The normal behavior was discussed earlier using Figure 6. These results for bare beryllium should be compared to those in Figure 16, which gives penetration data

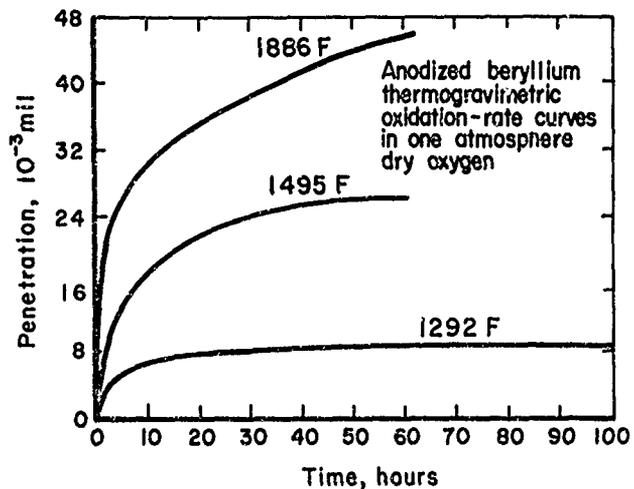


FIGURE 16. CALCULATED PENETRATION OF BERYLLIUM PROTECTED BY AN ANODIC FILM AT ELEVATED TEMPERATURE. (Reference 2)
Values are based on weight-gain data.

versus time for anodized beryllium specimens exposed at 1 atmosphere pressure of dry oxygen, at 1290, 1500, and 1890 F. The weight gains were reduced about 100 times by the anodic treatment.

No attack occurred on coated samples exposed to air with 1 percent moisture at 1470 F, for over 1000 hours.

Successful use of anodic coatings to prevent oxidation in components of SNAP 8 equipment was described by Nakae and Associates.⁽⁸⁵⁾

Five anodized specimens (transverse orientation) were exposed to a 5 percent salt spray at

room temperature at Southwest Research Institute. (86) One specimen showed noticeable attack in 240 hours. Five similar specimens exposed at 120 F were noticeably corroded in 24 hours.

Anodic coatings approximately 0.0002 inch thick were evaluated at Astropower. (7) The coatings were formed at 25 amp/ft² in 1 percent chromic acid and sealed by boiling in distilled water for 15 minutes. No corrosion was observed on specimens exposed to 5 percent salt fog spray at 100 F for 30 days. The corrosion specimens were also alternately exposed to 5 percent salt fog at 100 F for 16 hours and temperatures ranging up to 800 F for 8 hours.

The anodized coatings resisted chemical attack very well in the cyclic test at 200 F and 400 F. No deterioration of the coating could be detected by visual or microscopic observation. In the cyclic test at 600 F, a few white patches and a small amount of chipping were observed at the edges of the coupons after 14 cycles. All of the anodized coatings were severely attacked during cyclic tests at 800 F. High weight losses were observed with considerable color changes of the coatings. The beryllium coupons were rinsed in distilled water, and a spectrographic analysis of the distilled water showed traces of beryllium. Apparently, porous anodized coatings on beryllium are unstable when exposed to salt contamination and elevated temperature of 800 F. These tests showed that anodized coatings resist chemical attack due to salt contamination very well up to 600 F. At about 600 F, the anodized coatings become unstable when exposed to alternate salt contamination and elevated temperatures.

The effect of anodizing conditions on the protective properties of anodic coatings is summarized in Table 15 from Van Thyne. (68) The time for failure of bare beryllium is not given but it is stated that a 1/8-inch-thick specimen may oxidize completely in a few days at 1550 F in air at a dew point of 32 F. The conclusion from the studies reported in Table 15 was that chromic acid anodizing should be emphasized.

Work at Armour (87) indicated that anodic coatings as produced by Brush Beryllium were of value in protecting beryllium against 100 ppm of oxygen in helium at 1300-1410 F. It was estimated by extrapolation of data that a service life of 3000 hours at 1300 F might be expected.

Anodized beryllium was investigated to prevent or retard the interaction of beryllium

with UO₂ and corrosion by moist CO₂ at temperatures above 2192 F. (88) Better results were observed with chromic acid anodizing than with nitric-chromic acid anodizing. Reaction with UO₂ was avoided. Corrosion in moist CO₂ was reduced, but not consistently.

TABLE 15. ANODIZING CONDITIONS AND TIME TO FAILURE OF BERYLLIUM SPECIMENS EXPOSED AT 1450 F IN AIR^(a)
(Reference 68)

Anodizing Variables		Failure Time, hr
Temp.	Bath	
95 F	5N HNO ₃	260
Room	40%CrO ₃	279
41 F	40%CrO ₃	456
Room	10%Na ₂ Cr ₂ O ₇	260
Room	10%Na ₂ CrO ₄	360
105 F	10%NaOH	260
41 F	20%CrO ₃	456
Room	20%CrO ₃	528
Room	10%Na ₂ Cr ₂ O ₇	312

(a) Specimens were anodized at 100 amperes per square foot for 60 min. Dew point during exposure varied from +2 to +12 F.

As was mentioned elsewhere in this report anodized beryllium is compatible with dry and water-contaminated (5 percent) Aerozine-50. (37) The anodic coating was attacked by N₂O₄.

Sealing. There is some evidence that sealing processes are effective in improving the corrosion resistance of anodized coatings. Gilpin reported on a few tests conducted to show the effect of composition and sealing in boiling sodium silicate solution on the protection of forged beryllium when exposed to a 5 percent salt-fog spray at 100 F and elevated temperature of 600 F. (7) The current density was kept constant and bath compositions of 1, 3, and 6 percent CrO₃ were used. The anodizing temperature was 77 F and the sealing time in boiling water and sodium silicate solution was 15 minutes. Table 16 shows the results of these tests. Increasing the composition of the bath from 1 percent to 3 percent reduced the voltage to maintain a constant current density. This appeared to make an improvement on stability of porous anodized coatings. Sealing in boiling sodium silicate also showed beneficial effects.

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<p><i>7/6</i> This report summarizes the corrosion behavior of beryllium. The effects on beryllium of the following environments are considered: moisture, salt solutions, acids, alkalis, gases, organic liquids, molten materials, and solid materials. Stress-corrosion cracking and galvanic effects are also discussed. A final section of the report reviews various types of coatings for protection of beryllium from corrosion by a variety of environments.</p>		

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<p>Corrosion Stress-corrosion Protective coatings Surface treatments</p>						

INSTRUCTIONS

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