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THE CORROSION OF BERYLLIUM IN SIMULATED COOLING WATER FOR THE MATERIALS TESTING REACTOR

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REACTOR TECHNOLOGY DIVISION
Section IV - Engineering Materials

THE CORROSION OF BERYLLIUM IN SIMULATED COOLING WATER FOR THE MATERIALS TESTING REACTOR

James L. English

Date Issued

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TABLE OF CONTENTS

		Page
1.0	INTRODUCTION	7
2.0	ABSTRACT	8
3.0	STATEMENT OF THE PROBLEM	9
4.0	PART I - COMPARISON OF THE CORROSION RESISTANCE OF EXTRUDED AND QM SINTERED BERYLLIUM	9
	4.1 Test Materials and Treatment	9
	4.2 Description of Corrosion Test Method	12
	4.3 Test Results and Discussion	14
5.0	PART II - EXPANSION BETWEEN EXTRUDED BERYLLIUM INTERFACES	34
	5.1 Test Materials and Treatment	34
	5.2 Description of Corrosion Test Method	34
	5.3 Test Results and Discussion	39
6.0	ACKNOWLEDGEMENTS	44

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LIST OF TABLES

		Page
I	Chemical Analyses of Extruded and QM Types of Beryllium	11
II	Typical Analysis of Demineralized Water	13
III	Corrosion of Extruded Beryllium in Water	15
IV	Corrosion of Extruded Beryllium in 0.005M Hydrogen Peroxide	16
V	Corrosion of QM Beryllium in Water	17
VI	Corrosion of QM Beryllium in 0.005M Hydrogen Peroxide	18
VII	Comparison of the Corrosion Rate Between Extruded and QM Beryllium in Water and 0.0005M Hydrogen Peroxide	19
VIII	Chemical Analysis of Extruded Beryllium	39

LIST OF FIGURES AND PHOTOGRAPHS

		Page
1	A Comparison of the Maximum Pit Depth on Extruded and QM Beryllium in Water	21
2	A Comparison of the Maximum Pit Depth on Extruded and QM Beryllium in 0.005M Hydrogen Peroxide	22
3	A Comparison of the Pit Counts on Extruded and QM in Water	23
4	A Comparison of the Pit Counts on Extruded and QM Beryllium in 0.005M Hydrogen Peroxide	24
5	A Comparison of the Weight Losses on Extruded and QM Beryllium in Water	26
6	A Comparison of the Weight Losses on Extruded and QM Beryllium in 0.005M Hydrogen Peroxide	27
7	A Comparison of the Corrosion Rates on Extruded and QM Beryllium in Water	28
8	A Comparison of the Corrosion Rates on Extruded and QM Beryllium in 0.005M Hydrogen Peroxide	29
9	Frequency Distribution for Maximum Pit Depths Observed on Extruded and QM Beryllium Samples	31
10	Frequency Distribution for Number of Pits Observed on Extruded and QM Beryllium Samples	31
11	Photographs of Extruded and QM Beryllium Corrosion Specimens Exposed to Demineralized Water at 85°C	35
12	Photographs of Extruded and QM Beryllium Corrosion Specimens Exposed to Demineralized Water at 85°C	36
13	Photographs of Extruded and QM Beryllium Corrosion Specimens Exposed to 0.005M Hydrogen Peroxide at 85°C	37
14	Photographs of Extruded and QM Beryllium Corrosion Specimens Exposed to 0.005M Hydrogen Peroxide at 85°C	38
15	Separation of Beryllium - Beryllium Interfaces by Film Formation in 0.005M Hydrogen Peroxide at 85°C	41
16	Blister Formation on Extruded Beryllium After 480 Days Exposure in 0.005M Hydrogen Peroxide at 85°C	45

LIST OF FIGURES AND PHOTOGRAPHS (CONT'D)

Page

17 Blister Formation on Extruded Beryllium After 569 Days Exposure in 0.005M Hydrogen Peroxide at 85°C 46

18 Crack Formation on Extruded Beryllium After 569 Days Exposure in 0.005M Hydrogen Peroxide at 85°C 47

19 Blister Formation on Extruded Beryllium After 668 Days Exposure in 0.005M Hydrogen Peroxide at 85°C 48

20 Longitudinal View of Blister Formation on Extruded Beryllium After 668 Days Exposure in 0.005M Hydrogen Peroxide at 85°C 49

21-22-23 Enlarged Views of Corrosion Product Distribution on Extruded Beryllium Interfacial Surface 50, 51, 52

24-25 Corrosion Product Distribution on Extruded Beryllium Surfaces 53, 54

26 Photographs of Cleaned Extruded Beryllium Surfaces Showing the Extent of Localized Corrosion Attack 55

1.0 INTRODUCTION

This report is issued as Part I-B of a series of reports concerned with corrosion studies for the proposed Materials Testing Reactor by the Corrosion Group of the Reactor Technology Division at Oak Ridge National Laboratory*. Previous reports, Parts I and I-A have dealt with the corrosion of extruded and various types of powder processed beryllium. This present report deals with a comparison of the corrosion resistance of extruded vs. sintered beryllium tested over a period of one year as well as the general effect of long time exposure on extruded beryllium exposed to simulated reactor cooling water.

Inasmuch as these tests were started several years ago, they represent a comparative evaluation of beryllium metal available at that time. During this two year period, the technology of beryllium development and production has advanced accordingly, resulting in more pure and sound metal. Even so, the value of the investigation described in this period has not been lost since the extruded metal used throughout portions of the study has shown a corrosion resistance equal to that exhibited by present extruded beryllium.

*Other reports issued in this series include:

Part I: Interim Report on the Corrosion of Beryllium in Simulated Cooling Water for the Proposed Development Reactor, James L. English, ORNL 298, Mar. 16, 1949.

Part I-A Initial Corrosion Tests on Brush Process QM and QRM Beryllium, Arnold R. Olsen, ORNL 733, July 14, 1950.

Part II The Corrosion of 356 Aluminum in Simulated Cooling Water for the Proposed Materials Testing Reactor, James L. English, ORNL 681, July 20, 1950.

2.0 ABSTRACT

The corrosion resistance of extruded and QM types of beryllium metal was determined for a period of one year in demineralized water at 85°C with and without 0.005M hydrogen peroxide. In the absence of the peroxide, the corrosion resistance of the two materials was nearly identical; a value of 0.07 mil/year was observed at the end of the 12 months exposure. The presence of 0.005M hydrogen peroxide stimulated the corrosion rates for both metals with a more pronounced rate occurring on the QM beryllium. Corrosion rates of 0.17 mil/year and 0.33 mil/year were reported on extruded and QM beryllium, respectively, at the end of one year. Maximum pit depths on both metals were intensified with peroxide present but there was no marked increase in the frequency of pits on either metal. The QM beryllium appeared more susceptible to localized attack than did the extruded metal.

The expansion between adjacent extruded beryllium surfaces due to the accumulation of corrosion products was found to be 4.3 mils after 22.3 months in demineralized water at 85°C containing 0.005M hydrogen peroxide. The bond at the interfaces, formed by the corrosion products, was very tenacious. The appearance of large blisters on the beryllium surfaces after long exposure was believed due to the hydrolysis of segregated beryllium carbide inclusions to amorphous beryllium hydroxide. It was determined that this transition was accomplished by a large volume increase which may have caused sufficient internal pressures within the metal to result in the blistering effect.

3.0 STATEMENT OF THE PROBLEM

The immediate objectives of the beryllium corrosion study were two-fold, and are treated in Parts I and II of this report.

The first objective was to determine the relative corrosion resistance between good extruded beryllium and powder processed beryllium, Type QM, available at the time of test. This study was conducted to evaluate the corrosion resistance of the two types of beryllium for exposures of one year's duration in simulated cooling water for the Material Testing Reactor. The extruded beryllium used in these tests and previously exhibited good corrosion resistance to this medium in exposures not exceeding 60 days. The corrosion resistance of the materials over a longer period of time was unknown.

The second phase of the investigation was conducted to determine the amount of expansion that could occur between extruded beryllium interfaces exposed to simulated reactor cooling water conditions. The cause of this expansion, whether originating from the formation of films or corrosion products between these interfaces, or from other reasons, was to be determined. Also to be determined was the corrosion resistance of the extruded metal and the physical characteristics of the bond created between the interfaces by the formation of corrosion films.

4.0 PART I - COMPARISON OF THE CORROSION RESISTANCE OF EXTRUDED AND QM SINTERED BERYLLIUM

4.1 Test Materials and Treatment

Two types of beryllium were used in this study, extruded and QM beryllium.

The extruded beryllium metal was obtained from Massachusetts Institute of Technology in 1947. This material was received in the form of a 1 1/8 inch diameter bar, approximately 5 feet long. The bar was encased in a mild steel jacket which was removed by machining. The extrusion ratio of the bar was 16:1. Samples 1/4 inch in thickness and 1 inch diameter were machined from the bar. One hole, 1/4 inch diameter, was drilled in the center of each sample to furnish a means of support in the test medium. A chemical analysis of this material appears in Table 1.

The QM sintered beryllium metal (Y-4382BPQM) was procured from the Brush Beryllium Company in the form of small slabs having the following dimensions: 3/16" x 1 1/16" x 2". A hole, 1/4 inch diameter, was drilled near the end of each specimen. The QM metal was prepared by remelting Technical grade beryllium lump or pebbles. The remelting process with flux removes a greater portion of the residual magnesium from the original magnesium reduction operation, and results in a higher assay product and higher quality metal. A chemical analysis of this material is included in Table I.

4.1 Test Materials and Treatment (con't)

All test samples were polished on No. 80 and 120 emery papers, respectively, to remove surface defects and flaws. The samples were then cleaned in cold, 25% nitric acid for 20 minutes, rinsed in water, acetone, and alcohol, dried in an oven at 110°C for 20-30 minutes, and weighed prior to exposure. Surface areas were determined after the final polishing operation.

TABLE I

CHEMICAL ANALAYSES OF EXTRUDED AND QM TYPES OF BERYLLIUM

Element	Extruded Beryllium	QM Beryllium
Silver	0.0002 %	--
Aluminum	0.032	0.18 %
Calcium	0.002	--
Chromium	0.010	--
Copper	0.010	--
Iron	0.053	0.11
Magnesium	0.0056	0.05
Manganese	0.002	--
Sodium	0.002	--
Nickel	0.001	--
Silicon	0.0016	--
Tin	0.005	--
Zinc	0.005	--
Beryllium carbide	0.07	--
Assay (Total Be)	98.6	--
Beryllium oxide	~0.25	1.86

4.2 Description of Corrosion Test Method

Two types of test media were established to simulate cooling water conditions in the Materials Testing Reactor. Demineralized water was used throughout the tests. One solution contained 0.005M hydrogen peroxide to simulate the effects of irradiation on the water; the other solution contained no hydrogen peroxide.

Specimens were placed in glass jars containing 15 liters of water. The test jars were maintained at 85°C constantly in electrically heated water baths. The pH of the test water was adjusted daily, if necessary, within the range 5.5-6.5, by the use of dilute nitric acid or sodium hydroxide as the occasion demanded. The 0.005M concentration of hydrogen peroxide was maintained fairly constant by the addition of a determined amount of 4% hydrogen peroxide every 4 hours during the entire course of the test. Daily peroxide analyses were made. The water in the jars was discarded every week and replaced with fresh water. A water analysis appears in Table II as representative of the water quality during the course of the test.

Twelve samples of each type of beryllium were exposed to each solution. Samples were removed monthly for inspection of corrosion damage. This method of sample inspection was selected to furnish data on corrosion damage as a function of exposure time. The test was operated for one year with these conditions.

TABLE II

TYPICAL ANALYSIS OF DEMINERALIZED WATER USED IN CORROSION TESTS

Specific resistance, ohms/cm at 25°C	$4\text{-}6 \times 10^{-5}$
pH	5.5
Soap hardness ($CaCO_3$)	5.0 ppm
Dissolved CO_2	2.1 "
Dissolved solids	8.3 "
Non-volatile solids	6.1 "
Silicon dioxide	2.5 "
Iron	0.02 "
Aluminum	0.01 "
Copper	0.02 "
Nickel	0.05 "
Chromium	0.05 "
Calcium	0.12 "
Magnesium	0.16 "
Sodium	1.30 "
Sulfate	5.00 "
Chloride	0.50 "
Carbonate	2.10 "
Bicarbonate	4.20 "

4.3 Test Results and Discussion of Data

Corrosion data for the two types of beryllium exposed to demineralized water with and without 0.005M hydrogen peroxide are included in Tables III, IV, V, and VI. These results cover an exposure period of one year. An evaluation of the corrosion rates for the materials is included in Table VII.

Both materials showed moderate corrosion attack during the first 30 days of exposure indicating that this period is necessary for the development of a protective hydrated type of film similar to that formed on aluminum. A minimum corrosion rate for both types of beryllium was observed at the end of 120 days exposure in both types of test solution. The remaining 240 days showed fairly constant corrosion rates for both materials in demineralized water; the final value for both was 0.07 mil/year. The final 240 days of test in the 0.005M hydrogen peroxide solution showed an acceleration of corrosion attack, most prominent of which appeared on the QM beryllium. The corrosion rate for extruded beryllium at the end of 360 days was 0.17 mil/year; the final value for the QM beryllium was 0.33 mil/year or nearly double that of the extruded beryllium.

A more detailed discussion of the corrosion data follows, and Figures 1 to 8 show maximum pit depths, pit counts, weight losses, and corrosion rates as a function of the exposure time.

TABLE III

THE CORROSION OF EXTRUDED BERYLLIUM IN DEMINERALIZED WATER AT 85°C

Exposure Time, days	Max. Pit Depth, mils	Pit Count, no./cm^2	Wt. Loss, mdm*	Corrosion Rate, mil/year
30	1.4	0.4	3.7	0.10
60	4.0	2.2	2.7	0.07
90	8.0	1.2	1.1	0.03
120	8.0	4.0	1.2	0.03
150	1.4	2.4	1.4	0.04
180	1.4	3.2	2.7	0.07
210	2.8	0.6	4.0	0.10
240	1.7	2.4	2.8	0.07
270	12.8	2.1	5.0	0.13
300	16.4	3.1	3.8	0.10
330	0.8	4.4	2.6	0.07
360	10.0	2.8	2.8	0.07

Average specimen area 13.0 cm^2

*mdm is mg/dm^2/month

TABLE IV

THE CORROSION OF EXTRUDED BERYLLIUM IN DEMINERALIZED WATER CONTAINING 0.005M HYDROGEN PEROXIDE AT 85°C

Exposure Time, days	Max. Pit Depth, mils	Pit Count, no./cm^2	Wt. Loss, mdm	Corrosion Rate, mil/year
30	1.6	2.9	4.0	0.10
60	4.8	2.3	4.1	0.11
90	1.2	5.3	3.5	0.09
120	3.3	2.0	0.8	0.02
150	7.2	1.5	1.6	0.04
180	5.8	2.0	3.9	0.10
210	7.2	0.5	4.4	0.11
240	7.2	1.3	5.6	0.14
270*	-	-	-	-
300	13.6	1.6	8.1	0.21
330	20.4	3.6	7.2	0.19
360	11.2	6.8	6.6	0.17

Average specimen area 13.0 cm^2
* Sample lost

TABLE V

THE CORROSION OF QM BERYLLIUM IN DEMINERALIZED WATER AT 85°C

Exposure Time, days	Max. Pit Depth, mils	Pit Count, no./cm^2	Wt. Loss, mdm	Corrosion Rate, mil/year
30	3.0	2.5	6.5	0.17
60	4.0	0.5	2.2	0.06
90	1.2	3.0	0.2	0.005
120	3.2	2.8	0.1	0.003
150	1.6	3.1	1.8	0.05
180	1.6	7.7	2.5	0.06
210	5.2	3.1	4.3	0.11
240	1.6	17.1	3.1	0.08
270	1.8	10.1	3.4	0.09
300	7.2	11.5	3.0	0.08
330	1.2	12.2	3.2	0.08
360	7.2	7.7	2.7	0.07

Average specimen area, 33.7 cm^2

TABLE VI

THE CORROSION OF QM BERYLLIUM IN DEMINERALIZED WATER CONTAINING 0.005M HYDROGEN PEROXIDE AT 85°C

Exposure Time, days	Max. Pit Depth, mils	Pit Count, no./cm^2	Wt. Loss, mdm	Corrosion Rate, mil/year
30	2.0	1.6	5.6	0.14
60	2.4	0.5	1.2	0.03
90	2.4	1.0	0.2	0.005
120	3.7	1.7	0.1	0.003
150	4.8	2.0	3.7	0.10
180	6.0	6.1	6.6	0.17
210	4.4	0.9	7.5	0.19
240	7.6	5.0	6.8	0.18
270	9.6	8.5	13.2	0.34
300	12.8	9.6	12.8	0.33
330	12.8	9.6	11.3	0.29
360	16.0	5.6	12.9	0.33

TABLE VII

A COMPARISON OF THE CORROSION RATE OF EXTRUDED AND QM BERYLLIUM IN DEMINERALIZED WATER AT 85°C WITH AND WITHOUT 0.005M HYDROGEN PEROXIDE

Exposure Time, days	Corrosion Rate, mil/year			
	No Peroxide		0.005M Peroxide	
	Extruded	QM	Extruded	QM
30	0.10	0.17	0.10	0.14
60	0.07	0.06	0.11	0.03
90	0.03	0.005	0.09	0.005
120	0.03	0.003	0.02	0.003
150	0.04	0.05	0.04	0.10
180	0.07	0.06	0.10	0.17
210	0.10	0.11	0.11	0.19
240	0.07	0.08	0.14	0.18
270	0.13	0.09	--	0.34
300	0.10	0.08	0.21	0.33
330	0.07	0.08	0.19	0.29
360	0.07	0.07	0.17	0.33

4.3 Test Results and Discussion (Con't)

Figure 1 shows a comparison of the maximum pit depths observed on extruded and QM beryllium exposed to demineralized water at 85°C. The deepest pits appeared on the extruded metal and occurred at two points during the course of the test; during the 3 to 4 months exposure and during the 8 to 10 months exposure period. During the first mentioned period, the maximum pit depth was 8 mils; during the second exposure period, the maximum pit depth was 16.4 mils. Pit depth measurements on the sintered beryllium were not as severe and the maximum depth, 7.2 mils, was observed after an exposure of 10 months.

A comparison of the maximum pit depths on the test materials exposed to 0.005M hydrogen peroxide solution at 85°C is shown in Figure 2. In this case, the pit depths showed definite tendencies to increase with increased exposure time. The deepest pits were found on the extruded beryllium. After 10 months exposure, a pit depth of 20.4 mils was measured on the extruded metal. The maximum pit depth on the QM beryllium was 16 mils and occurred after the full exposure time, 12 months.

The number of pits counted on the samples exposed to demineralized water is reported in Figure 3. The most frequent occurrence of pits appeared on the QM beryllium, and was especially pronounced after passing the 6 months exposure time. The greatest number of pits was counted on a specimen exposed for 8 months; this value was 17.1 pits per cm^2. The greatest number of pits on the extruded beryllium was 4.4 pits per cm^2 and occurred after 11 months exposure. It was definitely concluded by these results that the susceptibility of QM beryllium to pitting attack was much greater than on extruded beryllium. The addition of 0.005M hydrogen peroxide to the water stimulated the frequency of pit formation on the extruded beryllium during the first 6 months of test. This period was followed by a gradual decline in the number of pits per cm^2 for 4 months and then the number increased until a maximum value of 6.8 pits per cm^2 was counted at the end of 12 months. Pitting frequency on the QM beryllium was more pronounced after the 4 months point was passed. A value of 9.6 pits per cm^2 after 10 months was recorded. In general, however, the frequency of pits on this material was not as great as that observed on specimens exposed to demineralized water. The presence of 0.005M peroxide, summarizing, stimulated the frequency of pit distribution on extruded beryllium and slightly decreased the frequency on QM beryllium as compared to results in water free of hydrogen peroxide. Figure 4 shows a graphic presentation of the frequency of pitting attack on the materials in 0.005M hydrogen peroxide solution at 85°C.

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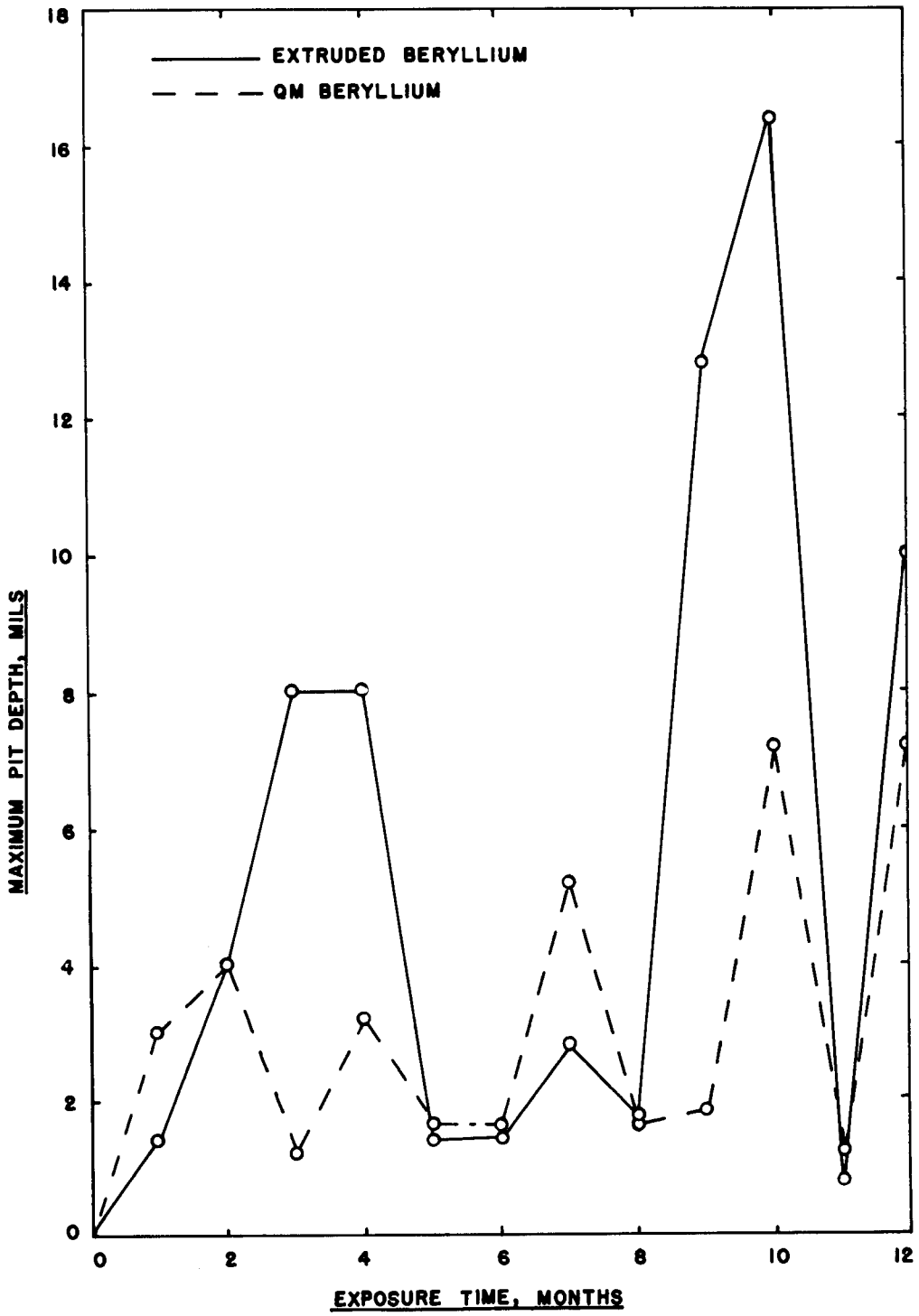

FIG. 1 A COMPARISON OF THE MAXIMUM PIT DEPTH ON EXTRUDED AND QM BERYLLIUM IN DEMINERALIZED WATER AT 85°C

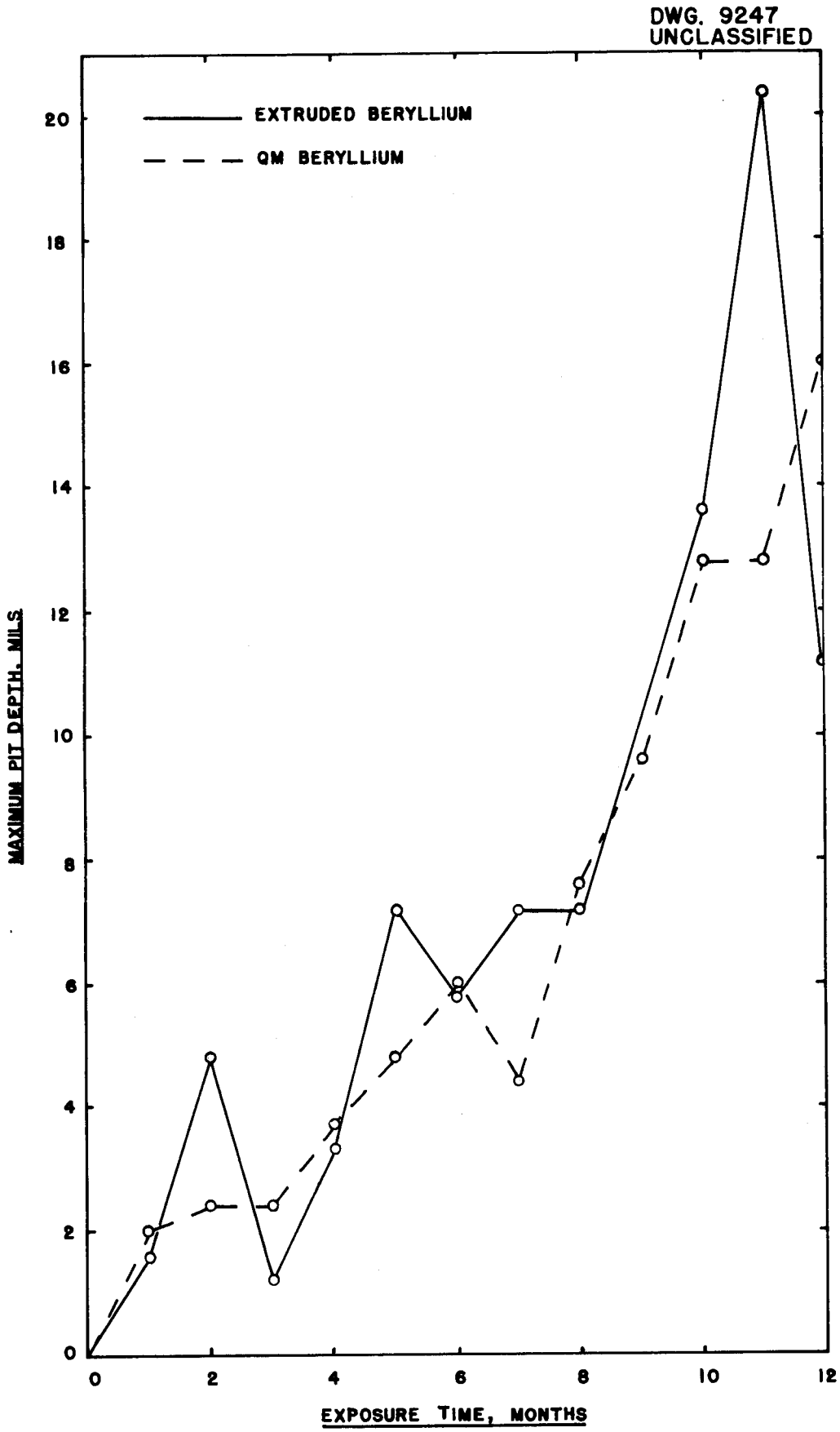

FIG. 2 A COMPARISON OF THE MAXIMUM PIT DEPTH ON EXTRUDED AND QM BERYLLIUM IN 0.005M HYDROGEN PEROXIDE AT 85°C

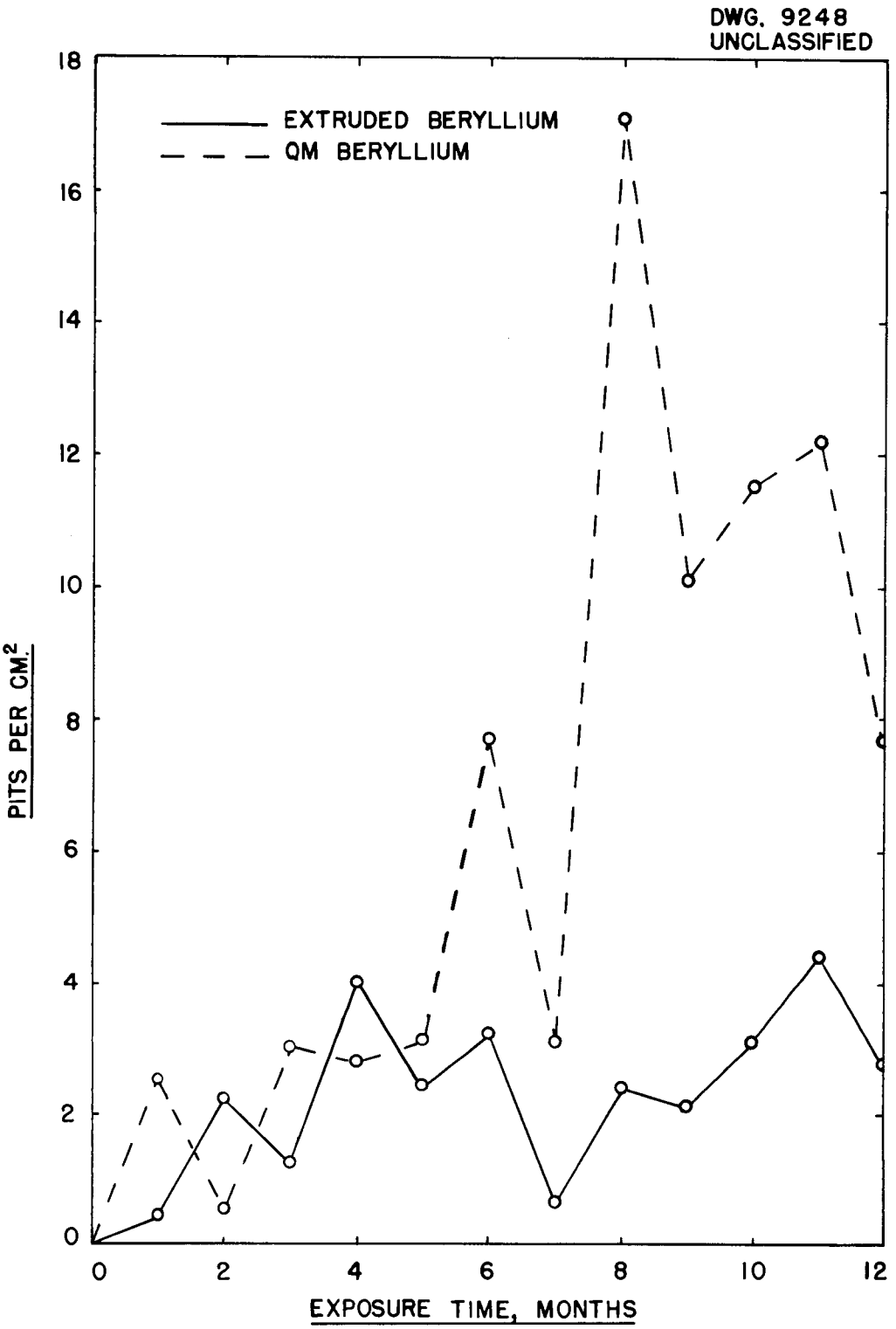

FIG. 3 A COMPARISON OF THE PIT COUNTS ON EXTRUDED AND QM BERYLLIUM IN DE-MINERALIZED WATER AT 85°C

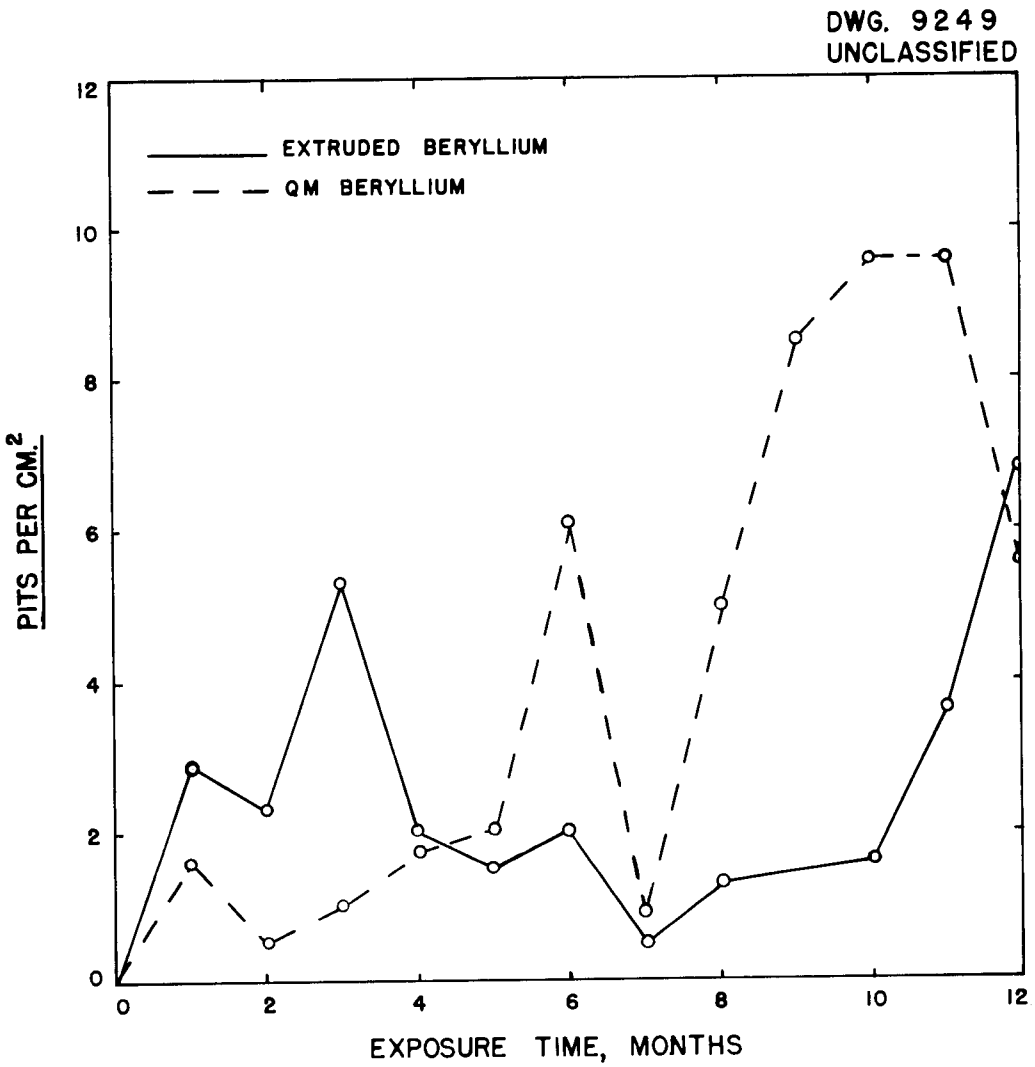

FIG. 4 A COMPARISON OF THE PIT COUNTS ON EXTRUDED AND QM BERYLLIUM IN 0.005 M HYDROGEN PEROXIDE AT 85° C

4.3 Test Results and Discussion (Con't)

Similar behavior was exhibited by both the extruded and sintered beryllium in demineralized water at 85°C in regard to the weight loss rates. These data are included in Figure 5 as a function of the exposure time. High initial weight loss rates were encountered. Then followed a period of 3 months in which the rates decreased markedly. From this point, the weight losses increased for 5 months after which another period of decreased losses occurred. At the end of 12 months exposure, the weight loss rate for the two materials was nearly the same, 2.8 $mg/dm^2/mo$. The addition of 0.005M hydrogen peroxide to the water, Figure 6, caused a slight suppression of the initial corrosion losses on both materials as compared to the previously mentioned test. A 3 month period of decreased weight losses followed after which the losses increased in a more linear fashion. The weight loss rates for QM beryllium after the first 4 months exposure were considerably higher than those for extruded beryllium after the same period of time. At the end of 12 months, the corrosion rate on the QM beryllium was 12.9 mdm as compared to 6.6 mdm on the extruded metal for the same time of exposure. The presence of hydrogen peroxide definitely stimulated the corrosion rate on the former.

Figure 7 and 8 show a summary of the corrosion rates for the two test materials in demineralized water and water containing 0.005M hydrogen peroxide. In the absence of hydrogen peroxide, the average corrosion rate for both metals was 0.07 mil/year. In the presence of peroxide, the corrosion rates for both materials increased; a value of 0.33 mil/year was obtained on QM beryllium as compared to 0.17 mil/year on extruded beryllium. It should be emphasized that all of these corrosion rates are extremely small and actually represent excellent corrosion resistance for both types of beryllium.

These data show that oxygen, when present in excess over the amount necessary to maintain and repair the protective hydrated oxide film formed on beryllium, can readily become a stimulator of corrosion attack. The appearance of the specimens indicated that the increased corrosion rate with excess oxygen manifested itself in the form of intensified localized attack. This was especially true for the QM beryllium.

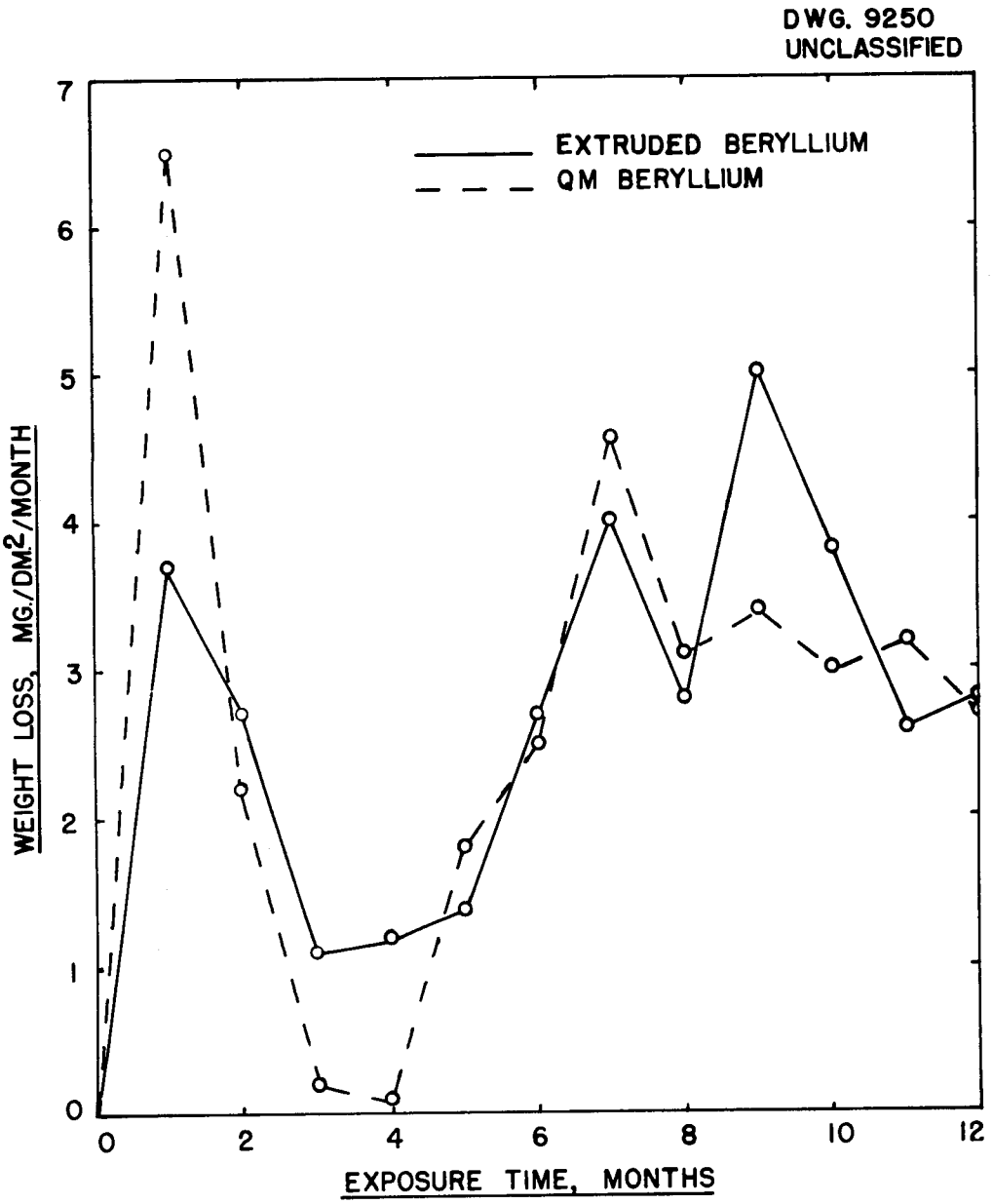

FIG. 5 A COMPARISON OF THE WEIGHT LOSSES ON EXTRUDED AND QM BERYLLIUM IN DEMINERALIZED WATER AT 85°C

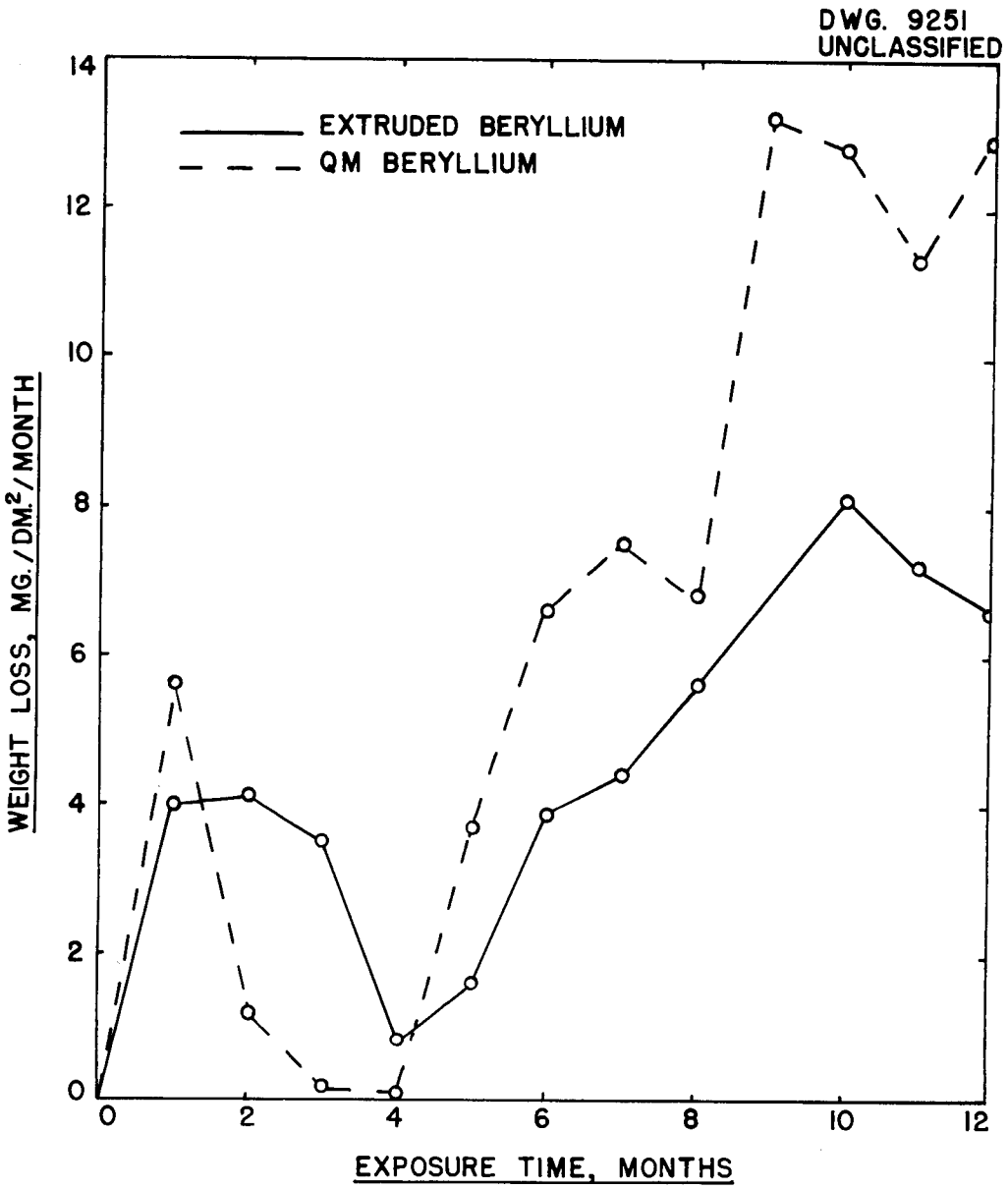

FIG. 6 A COMPARISON OF THE WEIGHT LOSSES ON EXTRUDED AND QM BERYLLIUM IN 0.005M HYDROGEN PEROXIDE AT 85° C

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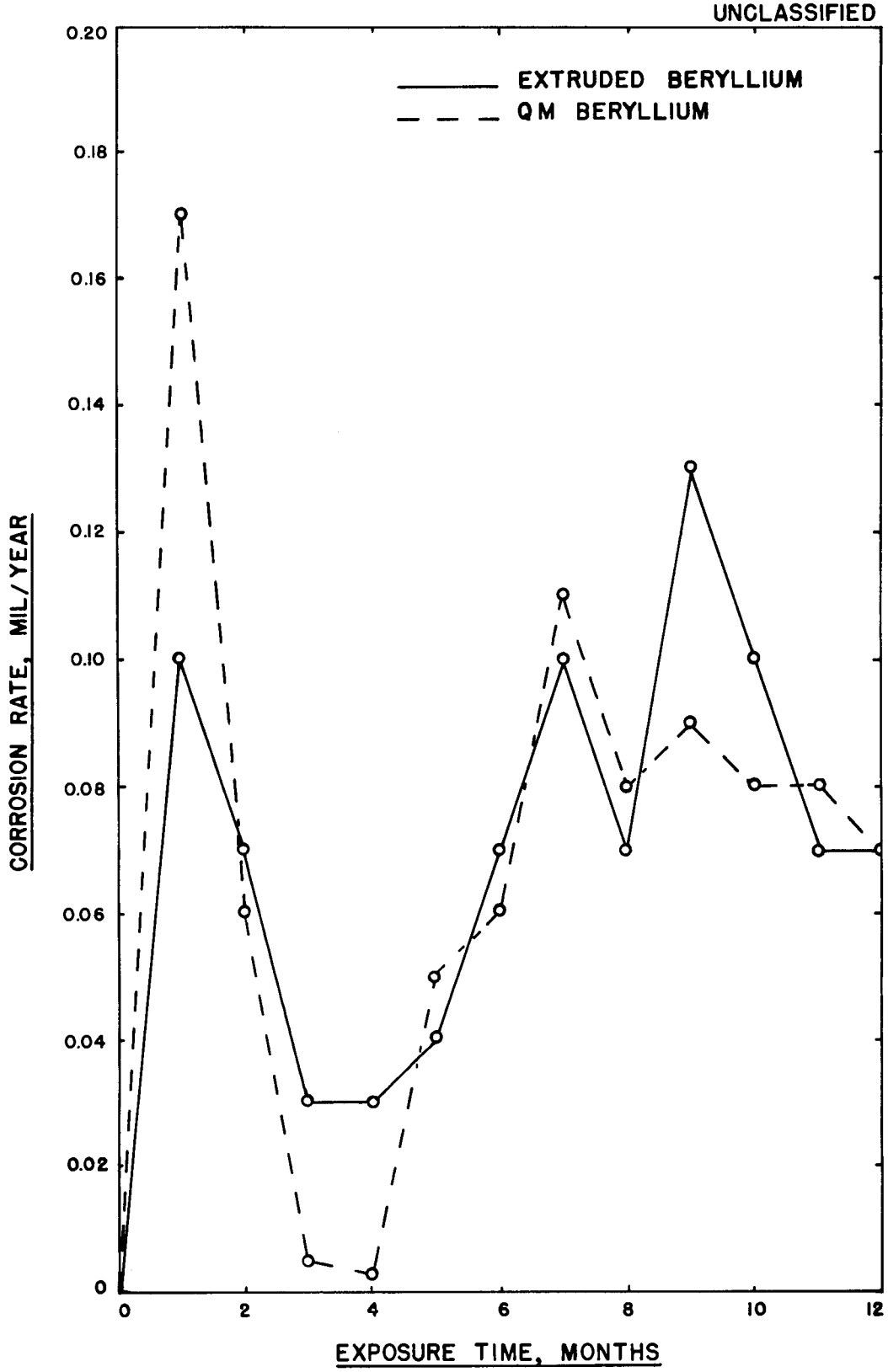

FIG. 7 A COMPARISON OF THE CORROSION RATES ON EXTRUDED AND QM BERYLLIUM IN DEMINERALIZED WATER AT 85°C

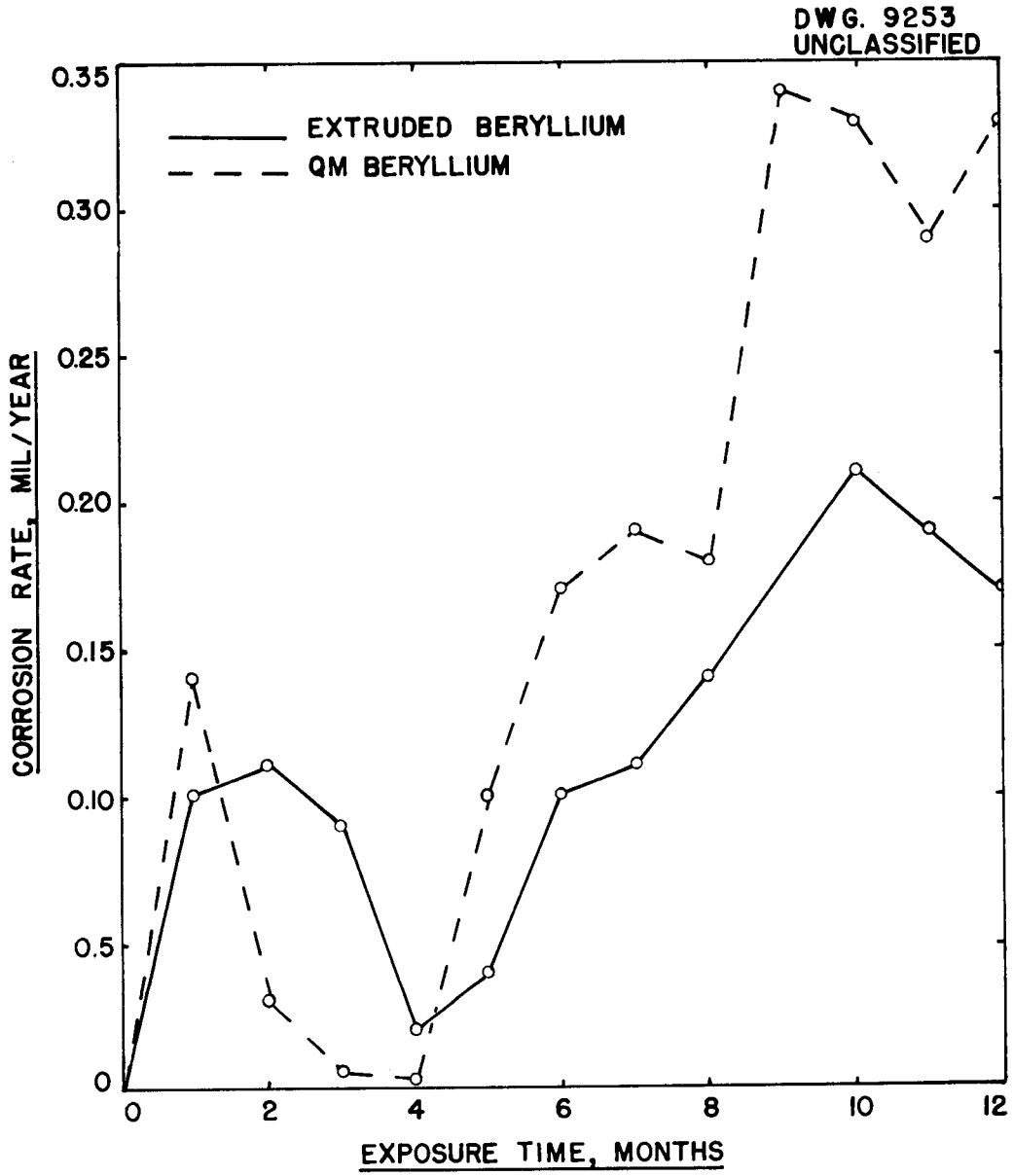

FIG. 8 A COMPARISON OF THE CORROSION RATES ON EXTRUDED AND QM BERYLLIUM IN 0.005 M HYDROGEN PEROXIDE AT 85°C

4.3 Test Results and Discussion (Con't)

Statistical methods of analysis were applied to certain sections of the corrosion data, namely, the maximum pit depths and the number of pits observed on the samples. In order to obtain a large group of observations for more accurate and representative analysis methods, the test results for the demineralized water and the water containing 0.005M hydrogen peroxide were combined. Figure 9 and 10 show grouped frequency histograms for the maximum pit depths and number of pits/cm^2 observed on QM and extruded beryllium samples. The greatest frequency of maximum pit depth for both materials was in the range of 0 to 2.5 mils. Thirty percent of the recorded maximum pit depths on extruded beryllium occurred between 0 and 2.5 mils; 17% occurred between 2.5 and 5.0 mils; 17% occurred between 5.0 and 7.5 mils and 8% were observed between 7.5 and 10.0 mils. The percentage occurring between 15 and 20 mils was 8 percent. On the QM beryllium, 38% of the maximum pit depths occurred between 0 and 2.5 mils; 25% occurred between 2.5 and 5.0 mils, and 17% fell between 7.5 and 10.0 mils. Approximately 70% of the maximum pit depths measured on both types of beryllium occurred between the range of 0 and 7.5 mils.

The most frequent occurrence of pit counts, number of pits per cm^2, ranged from 0 to 2.5 on both types of beryllium samples. These distributions are shown in Figure 10. This distriubtion was more pronounced on the extruded beryllium where 58% of the pits fell within this range. The distribution on the QM was more widespread where 30% of the pit counts came within the 0 to 2.5 pits/cm^2 range; 67% of the pit counts occurred between 2.5 and 12.5 pits/cm^2. No pit counts greater than 7.5 pits/cm^2 were found on the extruded beryllium.

Average values for the maximum pit depth and the pit counts were determined for the test materials in the two test media. Standard deviations were also determined from these test data. The nomenclature used for these calculations appears below.

$\bar{X}_1$ = the average value for maximum pit depth, mils

σ_1 = the standard deviation of the average value for maximum pit depth, mils

$\bar{X}_2$ = the average value for pit count, pits/cm^2

σ_2 = the standard deviation of pit count, pits/cm^2

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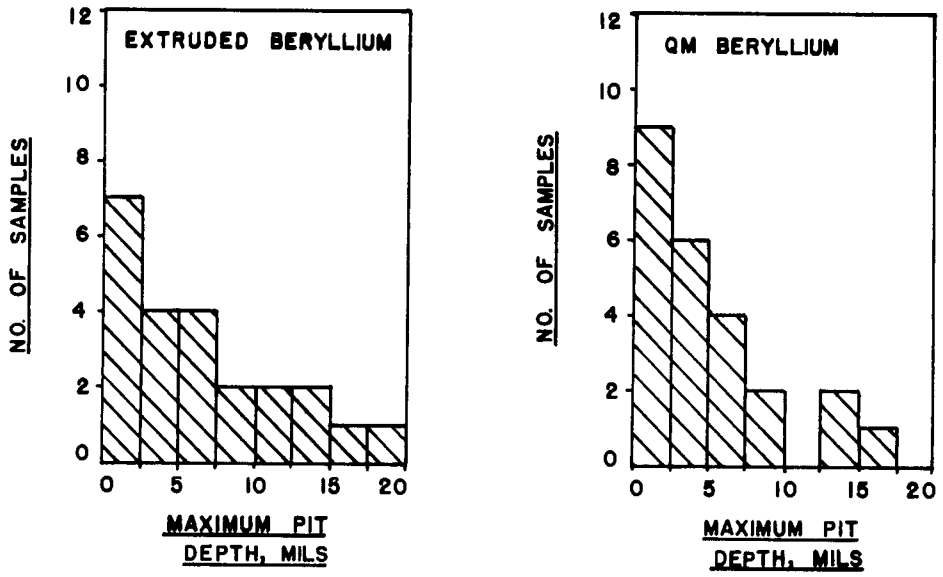

FIG. 9 FREQUENCY DISTRIBUTION FOR MAXIMUM PIT DEPTHS OBSERVED ON EXTRUDED AND QM BERYLLIUM SAMPLES

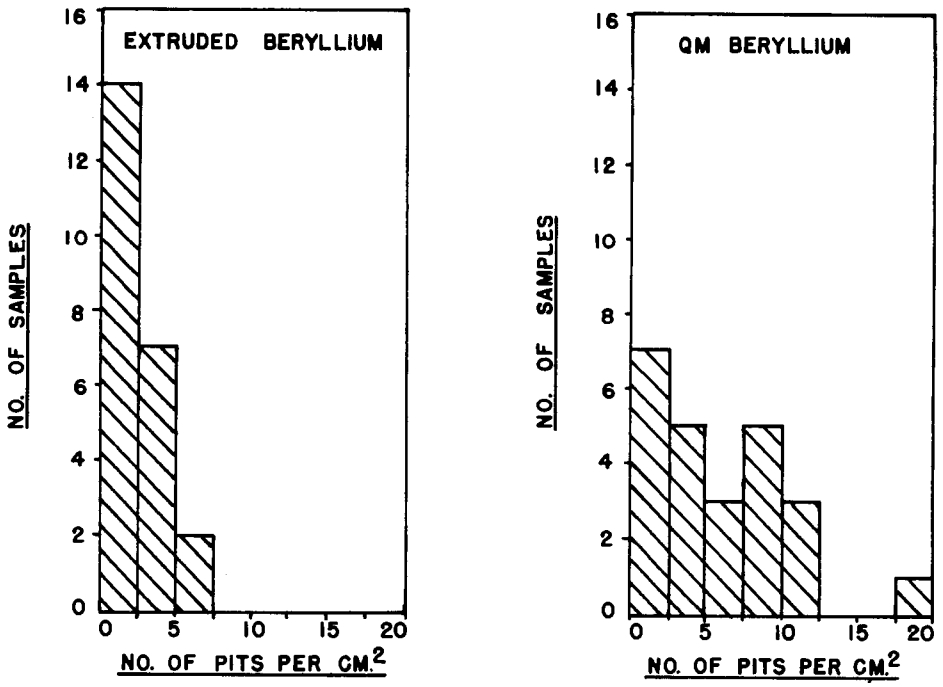

FIG. 10 FREQUENCY DISTRIBUTION FOR THE NUMBER OF PITS OBSERVED ON EXTRUDED AND QM BERYLLIUM SAMPLES

4.3 Test Results and Discussion (Con't)

The results of the statistical analysis are shown in the following table.

Material	Medium	$\bar{X}_1$	σ_1	$\bar{X}_2$	σ_2
Extruded Be	demineralized water	5.7	5.0	2.4	1.1
Extruded Be	0.005M peroxide	7.6	5.4	2.7	1.9
QM Be	demineralized water	3.2	2.2	6.8	4.9
QM Be	0.005M peroxide	7.0	4.6	4.3	3.3

Sample Calculation for Average and Standard Deviation (Table III)

Test Specimen	Max. Pit Depth, mils, (X_1)	Square of Max. Pit Depth, (X_1^2)
1	1.4	1.96
2	4.0	16.00
3	8.0	64.00
4	8.0	64.00
5	1.4	1.96
6	1.4	1.96
7	2.8	7.84
8	1.7	2.89
9	12.8	163.84
10	16.4	268.96
11	0.8	0.64
12	10.0	100.00
n = 12	$\Sigma X_1 = 68.7$	$\Sigma X_1^2 = 694.05$

$$\bar{X}_1 = \frac{\Sigma X_1}{n} = \frac{68.7}{12} = \underline{5.7 \text{ mils}}$$

$$\sigma_1 = \sqrt{\frac{\Sigma X_1^2}{n} - \bar{X}_1^2}$$

$$= \sqrt{\frac{694.05}{12} - 32.49}$$

$$= \sqrt{25.35}$$

$$= \underline{5.03 \text{ mils}}$$

[redacted]

4.3 Test Results and Discussion (Con't)

The average maximum pit depth increased for both the extruded and the QM types of beryllium when 0.005M hydrogen peroxide was added to the demineralized water test solution. The greatest increase occurred on the latter; the increase amounted to 120% over the value obtained in water containing no peroxide. The increase in depth for the extruded beryllium was approximately 33% when hydrogen peroxide was present. The standard deviation, a measure of the spread of the distribution, also increased when peroxide was added to the water. The increase of standard deviation was slight for the extruded beryllium but was more than doubled for the QM beryllium.

The number of pits per sq cm increased slightly on the extruded beryllium with hydrogen peroxide present, and decreased on the QM metal in the presence of peroxide. The standard deviation followed the same pattern on both materials.

These results show that oxygen is an intensifier of localized corrosion attack once such attack has started but it does not appear to simulate the frequency of pit formation on beryllium.

The results of this investigation on the relative corrosion resistance of extruded and QM beryllium may be summarized by the following statements.

1) The corrosion resistance of extruded and QM beryllium in demineralized water at 85°C containing no hydrogen peroxide is much the same, 0.07 mil/year for both materials, except that the initial rate of corrosion is higher for the QM metal than the extruded beryllium.

2) The presence of 0.005M hydrogen peroxide stimulates the corrosion rates for both extruded and QM beryllium. The magnitude of this acceleration is greater on QM metal. Corrosion rates of 0.17 and 0.33 mil/year were observed on extruded beryllium and QM beryllium, respectively, at the end of 12 months exposure.

3) The average maximum pit depth and the standard deviation were increased on both metals when hydrogen peroxide was added to the test solution. The maximum pit depth on extruded beryllium in untreated water was 16.4 mils; in water containing 0.005M peroxide, the maximum pit depth was 20.4 mils. The maximum pit depth on QM beryllium exposed to untreated water was 7.2 mils; this value increased to 16.0 mils in the presence of hydrogen peroxide.

4) A slight increase in the frequency of pit distribution was observed on extruded beryllium when peroxide was present; a noticeable decrease was reported on the frequency of pits on QM beryllium exposed to similar conditions. The standard deviation increased slightly

4.3 Test Results and Discussion (Con't)

for the extruded beryllium and decreased for the QM beryllium.

Photographs of the extruded and QM beryllium corrosion test specimens are shown in Figures 11, 12, 13, and 14.

5.0 PART II - EXPANSION BETWEEN EXTRUDED BERYLLIUM INTERFACES

5.1 Test Materials and Treatment

This test to determine the amount of expansion occurring between adjacent beryllium interfaces due to the formation of corrosion products has been described partially in ORNL-298 entitled " An Interim Report on the Corrosion of Extruded Beryllium". A brief review of the test method and description of specimens is presented in this report.

The vacuum cast and extruded beryllium used for the study was procured from Massachusetts Institute of Technology in 1947. The material was received in a bar form, approximately 2 3/4 inches square and had been extruded with a ratio of 6 to 1. A chemical analysis of the metal appears in Table VIII.

5.2 Description of Corrosion Test Method

The specimen arrangement consisted of 5 circular samples, 5 cm in diameter and 0.6 cm thick. One of the samples was machined from a solid piece of beryllium, 3 cm in length, so that a centerpost, 0.6 cm in diameter and 2.4 cm in length was obtained at the center of the circular specimen. The end of this centerpost was threaded to a depth of 0.6 cm. Three of the specimens had 0.6 $\pm$ 0.002 cm holes drilled through centers and the fourth disc was tapped and internally threaded. By this arrangement, the specimens could be centered on the central post and hand tightened by threading the fifth disc onto the centerpost.

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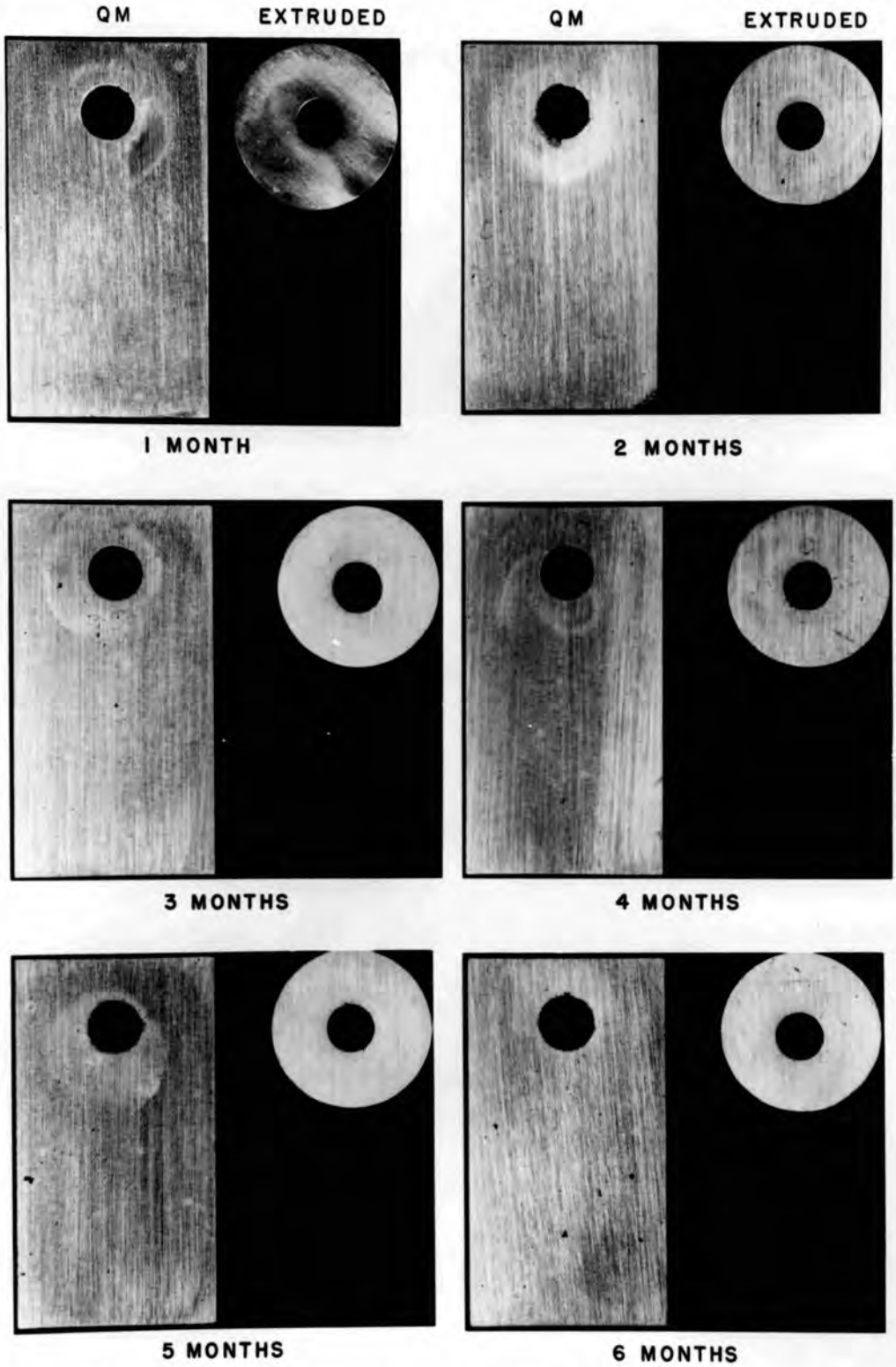

FIGURE II. QM AND EXTRUDED BERYLLIUM SAMPLES AFTER EXPOSURE TO DISTILLED WATER AT 85°(Mag.)

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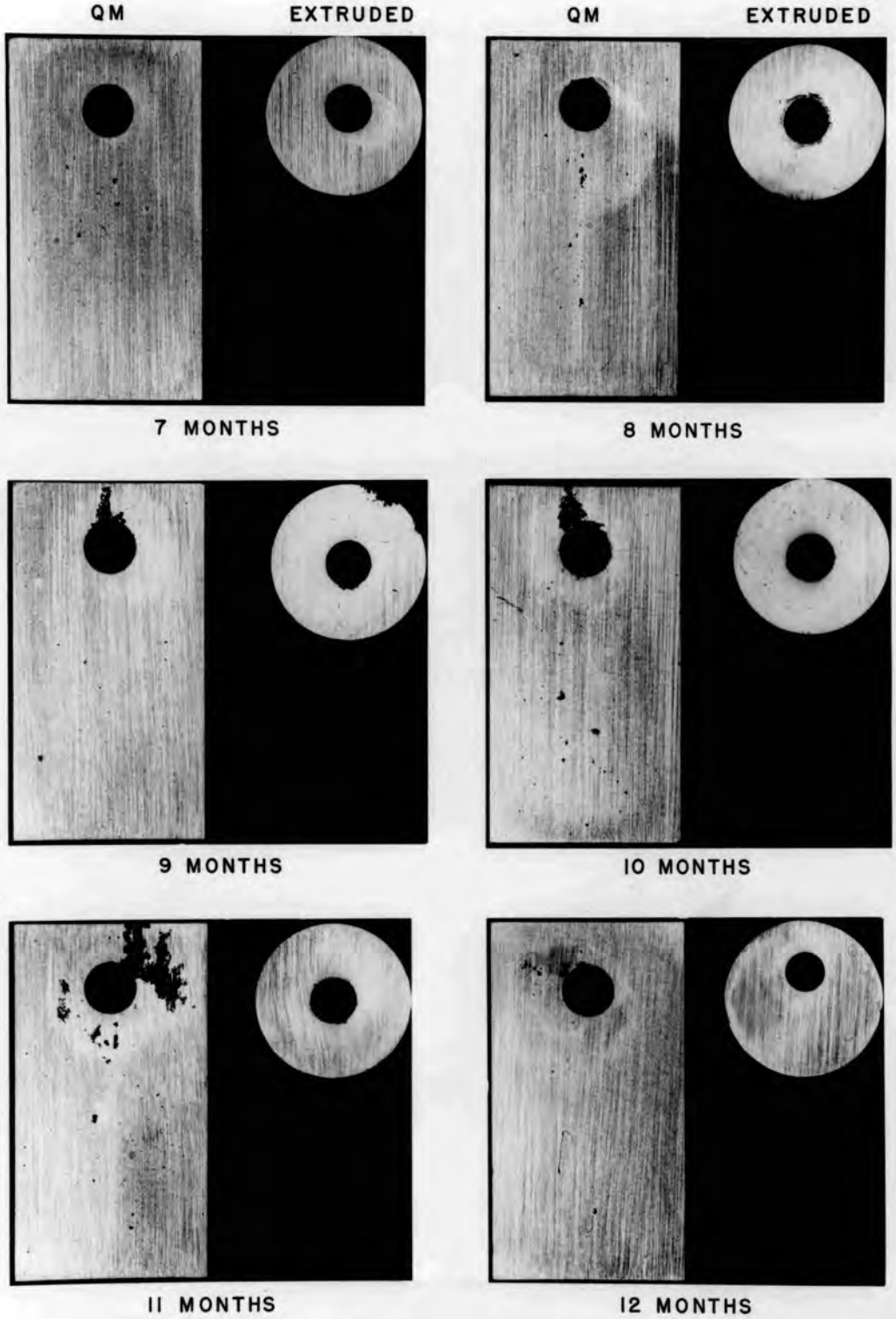

FIGURE 12. QM AND EXTRUDED BERYLLIUM SAMPLES AFTER EXPOSURE TO DISTILLED WATER AT 85° C (Mag.)

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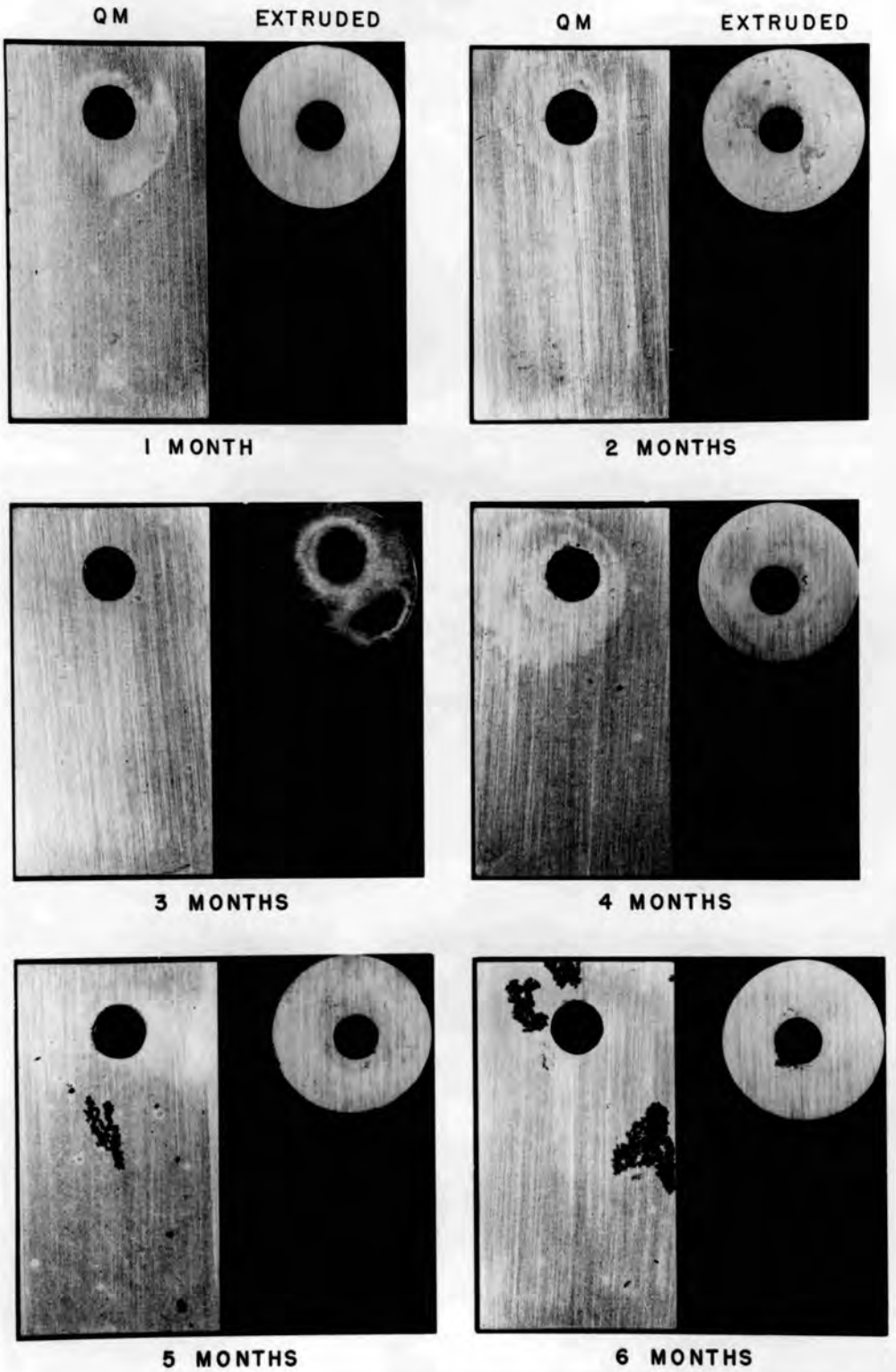

FIGURE 13. QM AND EXTRUDED BERYLLIUM CORROSION SAMPLES AFTER EXPOSURE TO 0.005 M HYDROGEN PEROXIDE AT 85° C (Mag.)

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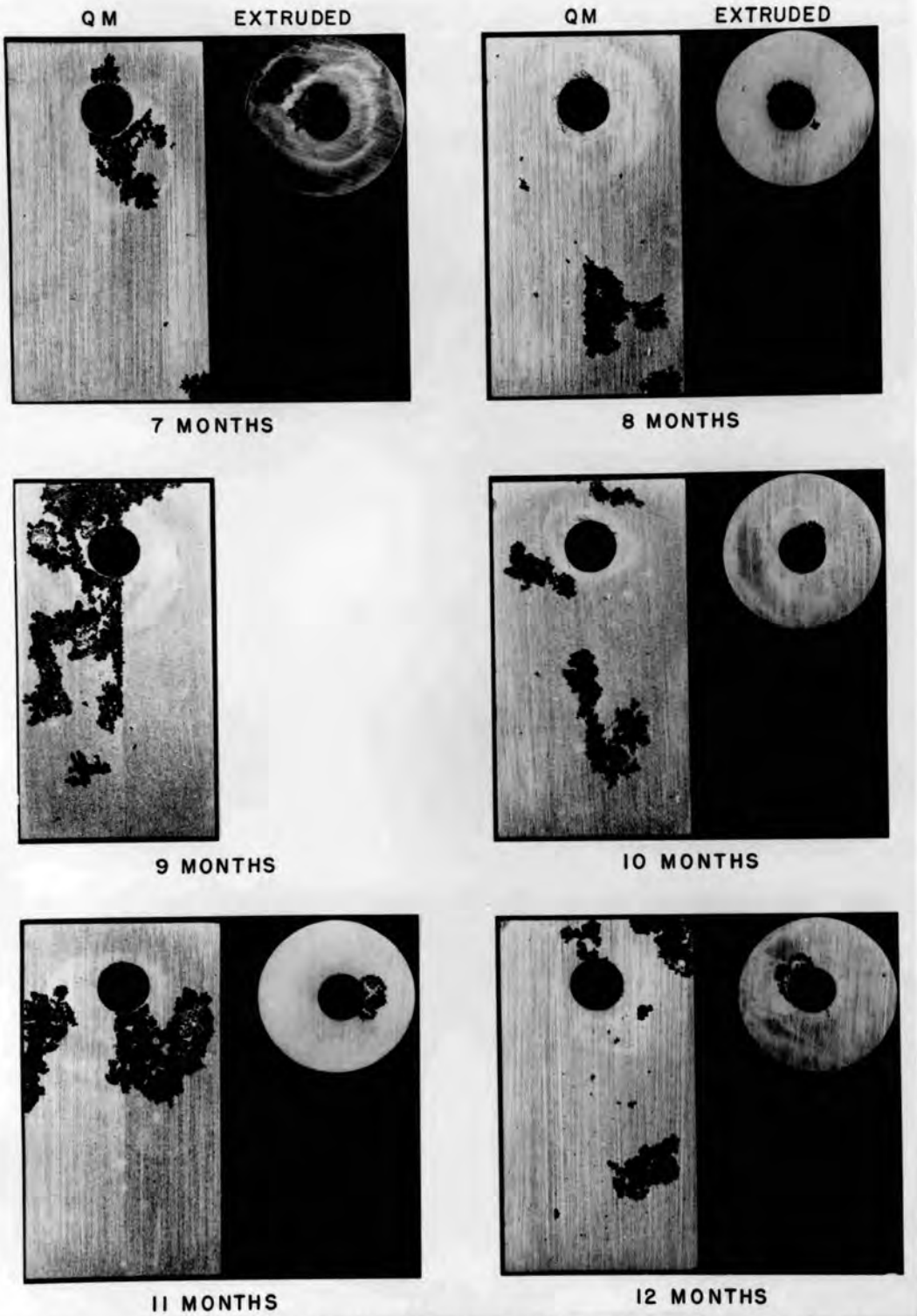

FIGURE 14. QM AND EXTRUDED BERYLLIUM CORROSION SAMPLES AFTER EXPOSURE TO 0.005 M HYDROGEN PEROXIDE AT 85°C (Mag.)

5.2 Description of Corrosion Test Method (Con't)

TABLE VIII

CHEMICAL ANALYSIS OF EXTRUDED BERYLLIUM

Aluminum	0.10 %
Calcium	0.005
Chromium	0.008
Copper	0.01
Iron	0.063
Manganese	0.003
Sodium	0.002
Nickel	0.002
Silicon	0.05
Tin	0.008
Zinc	0.005
Beryllium carbide	0.19
Assay (total Be)	97.8

The tightened specimens were adjusted so that equal thickness measurements, $\pm$ 0.001 cm, were obtained at four reference points spaced at 90°C intervals on the two outermost specimens. Prior to assembly, the specimens were cleaned in cold, 25% nitric acid, thoroughly washed in water, and dried.

The assembled unit, weighing 121.43 gm, was placed into 15 liters of demineralized water at 85°C containing 0.005M hydrogen peroxide. The water pH was maintained within the range of 5.5-6.5. Hydrogen peroxide additions were made every 3 hours during the course of the test in order to keep the concentration approximately at 0.005M. The water was agitated by means of an electrical stirrer.

5.3 Test Results and Discussion

The assembly was removed frequently and measurements were made at the four reference points to determine the average expansion between interfaces. These results for 668 days test are shown below and appear in Figure 15 plotted against the exposure time.

5.3 Test Results and Discussion (Con't)

Accumulative Exposure Time, days	Average Interfacial Expansion mils/interface
45	0.52
104	0.88
162	0.88
193	1.00
344	1.52
480	3.56
569	3.60
668	4.32

As observed from these data, a dormant period of expansion between interfaces existed during the first 193 days of exposure. The average expansion/interface at the end of this time was 1 mil. During the following 475 days of exposure the expansion of the assembly increased steadily to a value of 4.32 mils/interface. At this point, the test was stopped.

During the course of the test, the assembly was frequently removed for visual inspection. No significant developments were observed for 48 days. The assembly showed no signs of intensified corrosion attack although the outer surfaces were spottily coated with loosely-adherent white corrosion products. At the end of 480 days an abrupt increase of the expansion between interfaces was found. This value was 3.56 mils/interface, an increase of 2.04 mils/interface over the previously reported value at the end of 344 days. Also observed was another significant development in the form of a large, cracked blister on the side of the topmost specimen. This defect is shown in Figure 16. Adjacent to this large blister appeared a smaller, raised defect, which was not cracked. The crack on the large blister was 192 mils in length and the metal had been pushed to a height of 64 mils above the surrounding surfaces. The blister gave the appearance of being formed by expansion forces originating from some source within the internal structure of the metal near the surface.

The assembly was returned to the test solution and exposed for an additional 89 days. At the end of this time, a total of 569 days, a third blister was observed on the side of one of the other beryllium discs. This blister was 240 mils in diameter.

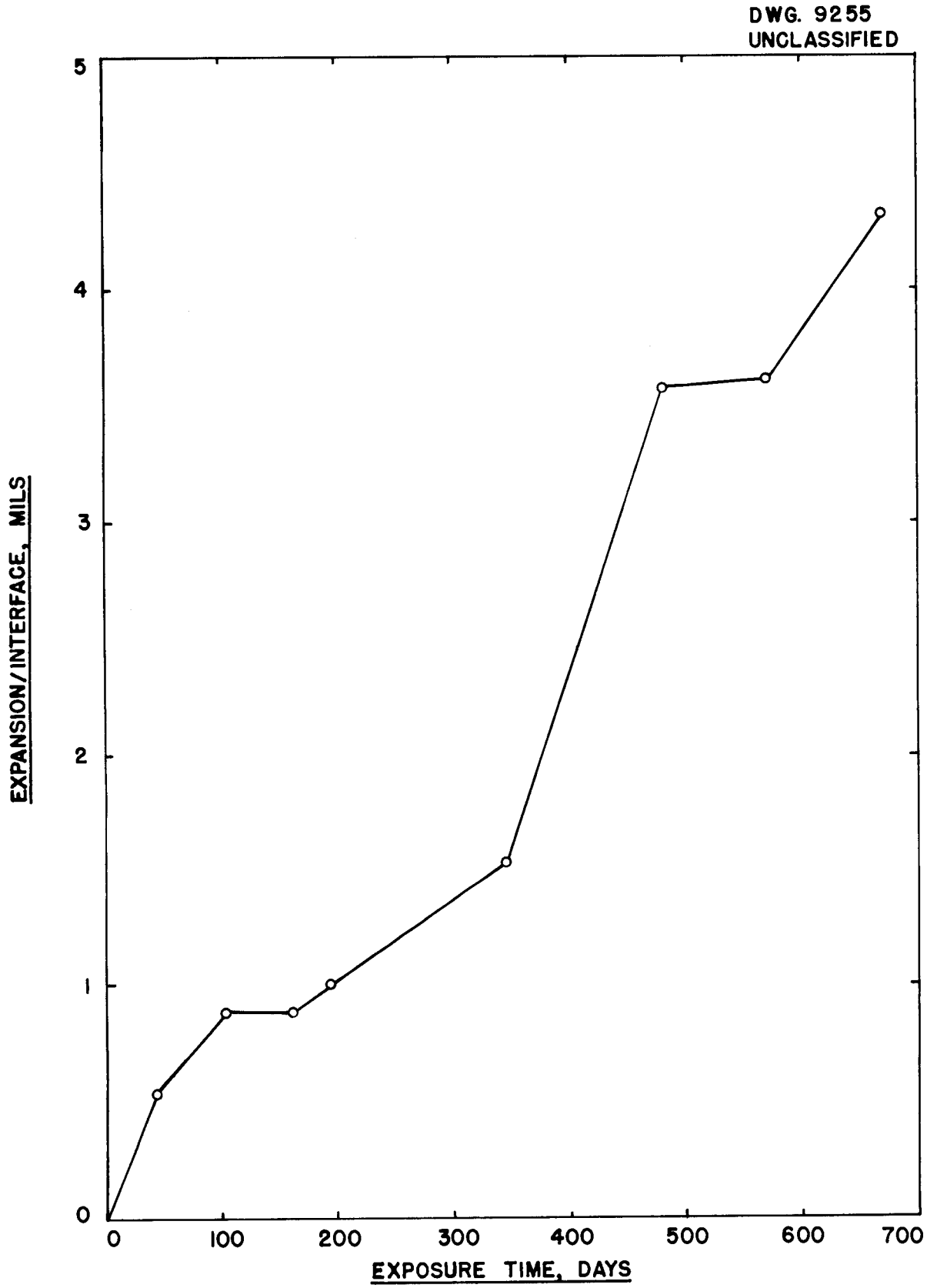

FIG. 15 THE EXPANSION OF BERYLLIUM INTERFACES EXPOSED TO 0.005M HYDROGEN PEROXIDE AT 85°C

5.3 Test Results and Discussion (Con't)

The original blister exhibited an increased growth and measured 220 mils diameter, an increase of 28 mils over the measurement recorded after 480 days. A photograph of the test assembly after 569 days exposure is shown in Figure 17.

Another significant development observed on the assembly was the presence of a crack, parallel to the extrusion direction which was located adjacent to the two blisters on the outermost beryllium disc. This crack extended for 280 mils across the face of the beryllium, i.e., from the edge of the specimen to the end point of the crack. Figure 18 shows a photograph of the crack formation appearing after 569 days of exposure.

The specimen assembly was returned to test for an additional 99 days. At the end of this period, the average expansion per interface was 4.32 mils. The large blister showed continued growth and had cracked in numerous spots across its raised surfaces. A photograph is shown in Figure 19. Three smaller new blisters were observed on other beryllium side surfaces. A longitudinal view showing the height of the large blister above the surrounding metal appears in Figure 20 after 668 days. The height of this blister was nearly 100 mils. After a total of 668 days, the test was stopped. The weight of the assembled unit as removed from the solution and dried, showed an increase of 2.0 gm over the original weight of 121.43 gm. The separation of the beryllium discs was difficult and it was finally necessary to shear the 1/4 inch diameter centerpost by applying a steady torque with pipe wrenches. None of the specimens could be turned on the centerpost without shearing the beryllium rod. It was very evident that the bond formed between interfaces was extremely tenacious due to the formation and accumulation of corrosion products.

White masses of corrosion products were spread spottily across the interfacial surfaces of the beryllium. Figures 21, 22, and 23 represent a typical appearance of corrosion product distribution on the specimens. Figures 24 and 25 are photographs, actual size, of the adjacent beryllium surfaces which constituted the four beryllium-beryllium interfaces. The arrangement of the corrosion product formations on the contacting surfaces indicates that the corrosion medium made intimate contact with the metal at nearly every point. The resulting effect was the formation of concentration cells, probably an oxygen type, due to stagnation of the liquid. Localized corrosion proceeded at these areas with the formation of insoluble corrosion products forming over and around pits.

5.3 Test Results and Discussion (Con't)

Samples of the white corrosion products between the interfaces were subjected to microscopic and X-ray examinations. This material was identified as an amorphous form of beryllium hydroxide. It was also found that large portions of the corrosion product resulted from a hydrolysis of beryllium carbide present in the metal. Work done by Wilmarth[1] showed that beryllium carbide, subjected to steam exposure, changed in color from a yellowish brown to a grayish white and had apparently undergone a volume expansion approximately four times greater than its original volume. Such a phenomenon could explain the formation of the large blisters observed on the beryllium test specimens. It appears reasonable that segregations of carbide inclusions on or very close to the surfaces could, after long exposures, undergo a change of volume due to hydrolysis effects, and cause internal pressures of sufficient magnitude to force the metal into a blistered condition. For a complete and excellent study of this effect, the reader is referred to the work of Wilmarth.[1]

The five specimens were cleaned in cold, 25% nitric acid to remove corrosion products. Extensive localized corrosion attack was disclosed beneath the corrosion products. Photographs of the cleaned surfaces are shown in Figure 26. The maximum pit depth recorded on these specimens was 10-15 mils. As encountered in previous corrosion studies with beryllium, localized corrosion attack exhibited a greater tendency to spread transversely across the metal surfaces rather than penetrate deeply into the metal.

The results of this investigation may be summarized in the following statements.

1) The maximum value for expansion between extruded beryllium interfaces exposed to 0.005M hydrogen peroxide at 85°C for 668 days was 4.32 mils.

2) The bond created between extruded beryllium interfaces by the formation of corrosion products was extremely tenacious and separation of interfaces was accomplished with great difficulty.

3) The formation of large blisters on extruded beryllium surfaces after long exposure to 0.005M hydrogen peroxide may possibly be due to the hydrolysis of beryllium carbide segregations to amorphous beryllium hydroxide. This transition is accompanied by a large volume increase which may be sufficient to create internal pressures great enough to cause the blistering effect.

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1 T. E. Wilmarth, Examination and Comparison of Fibrous Beryllium Displaying Various Flaws, ORNL CF-49-3-207, 3-17-49.

6.0 ACKNOWLEDGEMENTS

The writer wishes to express his sincere appreciation to personnel of the Oak Ridge National Laboratory for their contribution of effort to this investigation.

T. E. Wilmarth of the Chemistry Division for photographs and examination of corrosion products.

S. H. Wheeler, H. L. Barker, and J. W. Brown, of the Corrosion Laboratory-Reactor Technology Division, for their valuable assistance in the preparation and examination of test specimens, and preparation of graphs and photographs.

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PHOTO NO. 10231

FIGURE 16. BLISTER FORMATION ON EXTRUDED BERYLLIUM AFTER 480 DAYS IN 0.005 M HYDROGEN PEROXIDE AT 85°C (Mag.)

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10232

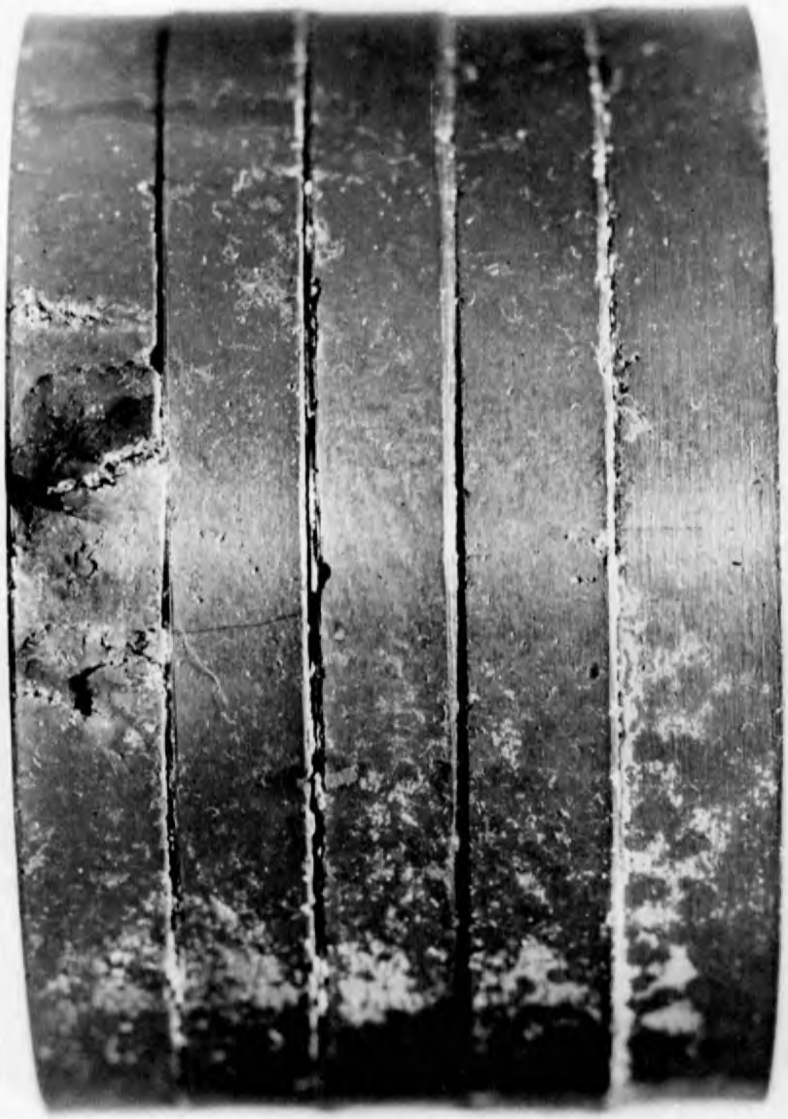

FIGURE 17. BLISTER FORMATION ON EXTRUDED BERYLLIUM AFTER 569 DAYS IN 0.005 M HYDROGEN PEROXIDE AT 85°C (Mag.)

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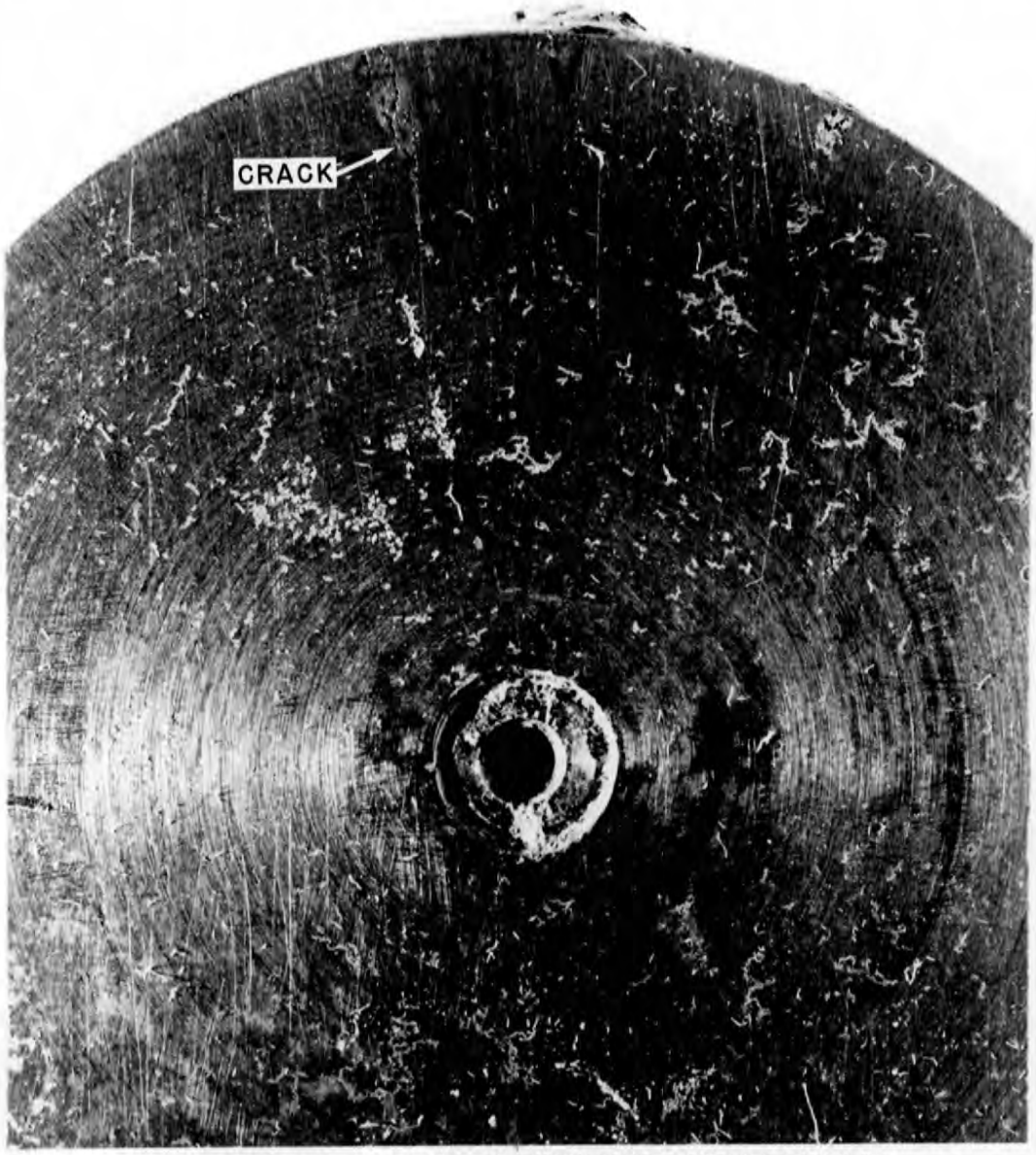

FIGURE 18. CRACK FORMATION ON EXTRUDED BERYLLIUM AFTER 569 DAYS IN 0.005M HYDROGEN PEROXIDE AT 85°C (Mag.)

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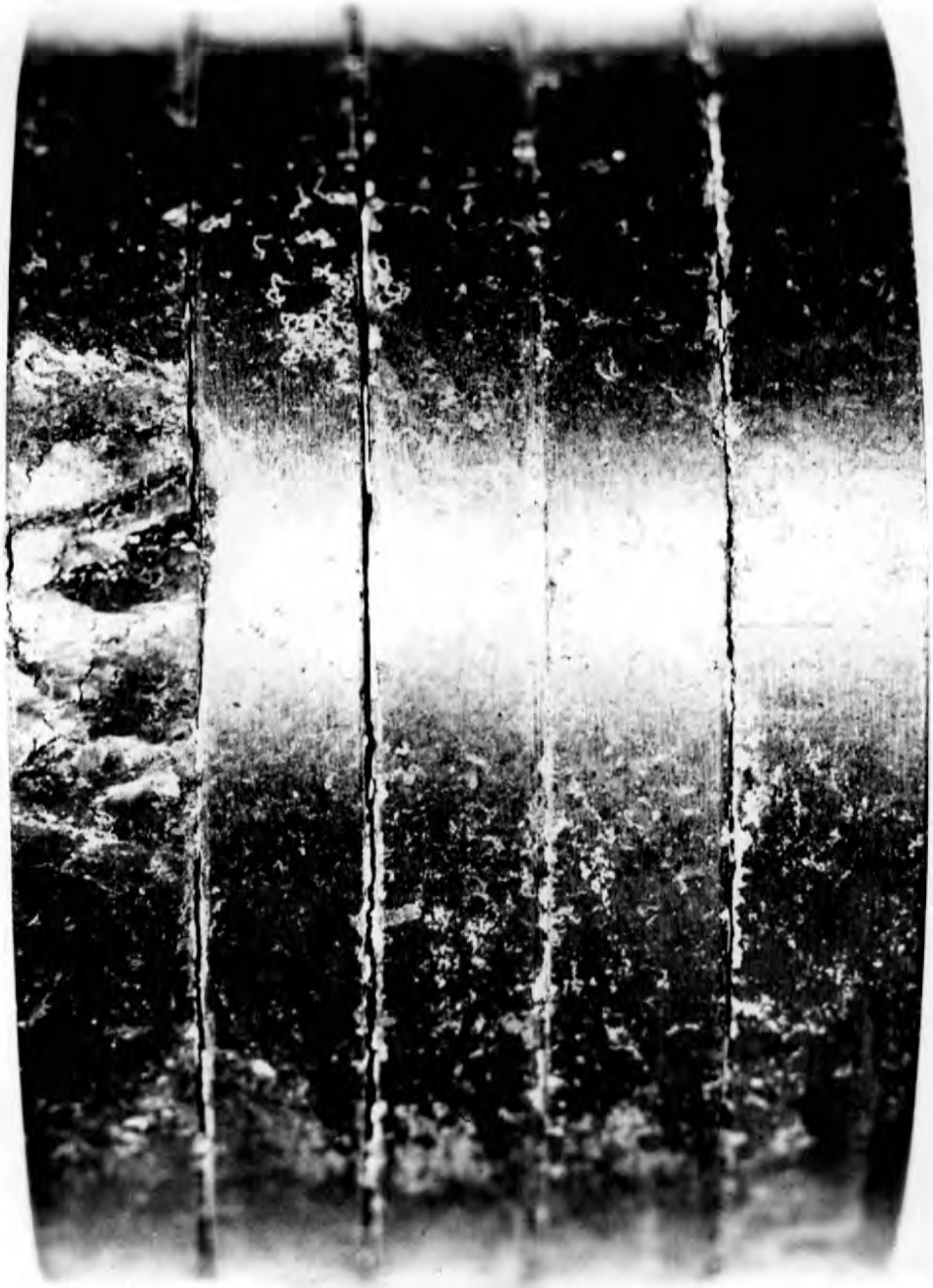

FIGURE 19. BLISTER FORMATION ON EXTRUDED BERYLLIUM AFTER 668 DAYS IN 0.005 M HYDROGEN PEROXIDE AT 85°C (Mag.)

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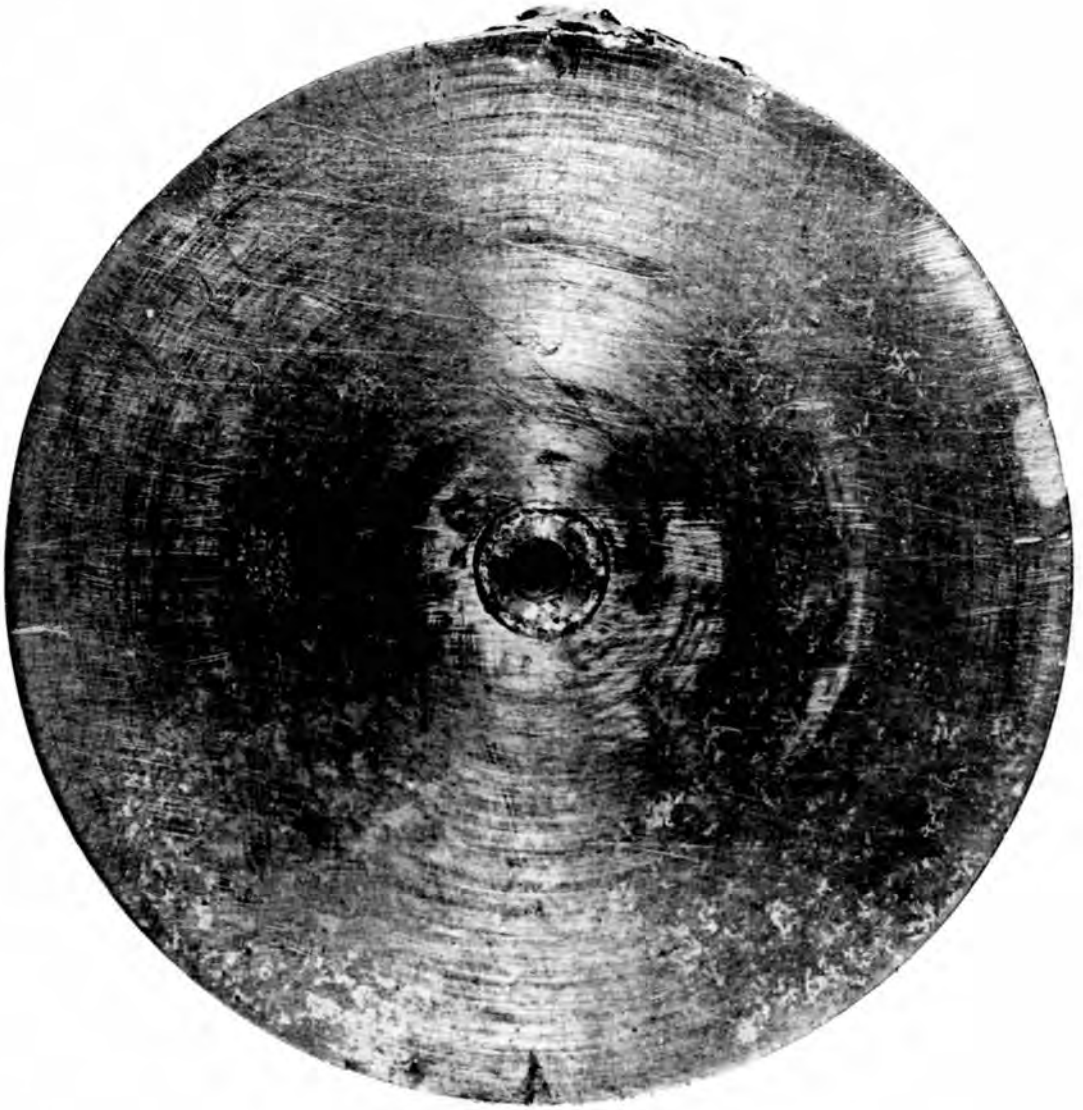

FIGURE 20. LONGITUDINAL VIEW OF BLISTER FORMATION ON EXTRUDED BERYLLIUM EXPOSED 668 DAYS IN 0.005 M HYDROGEN PEROXIDE (Mag.)

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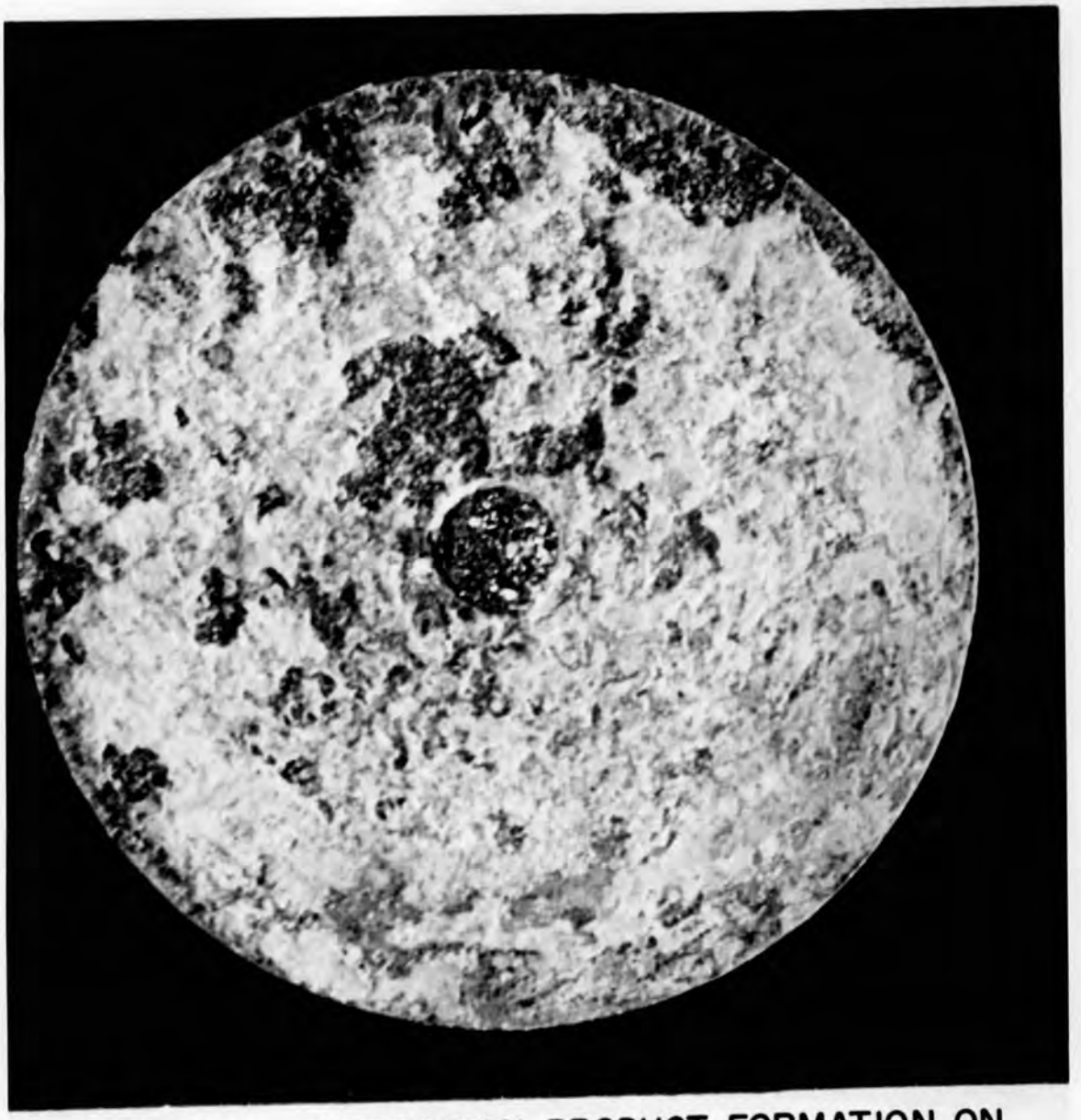

FIGURE 21. CORROSION PRODUCT FORMATION ON BERYLLIUM INTERFACE AFTER 668 DAYS IN 0.005 M HYDROGEN PEROXIDE AT 85°C (Mag.)

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FIGURE 22. CORROSION PRODUCT FORMATION ON BERYLLIUM INTERFACE AFTER 668 DAYS IN 0.005 M HYDROGEN PEROXIDE AT 85°C (Mag.)

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FIGURE 23. CORROSION PRODUCT FORMATION ON BERYLLIUM INTERFACE AFTER 668 DAYS IN 0.005 M HYDROGEN PEROXIDE AT 85°C (Mag.)

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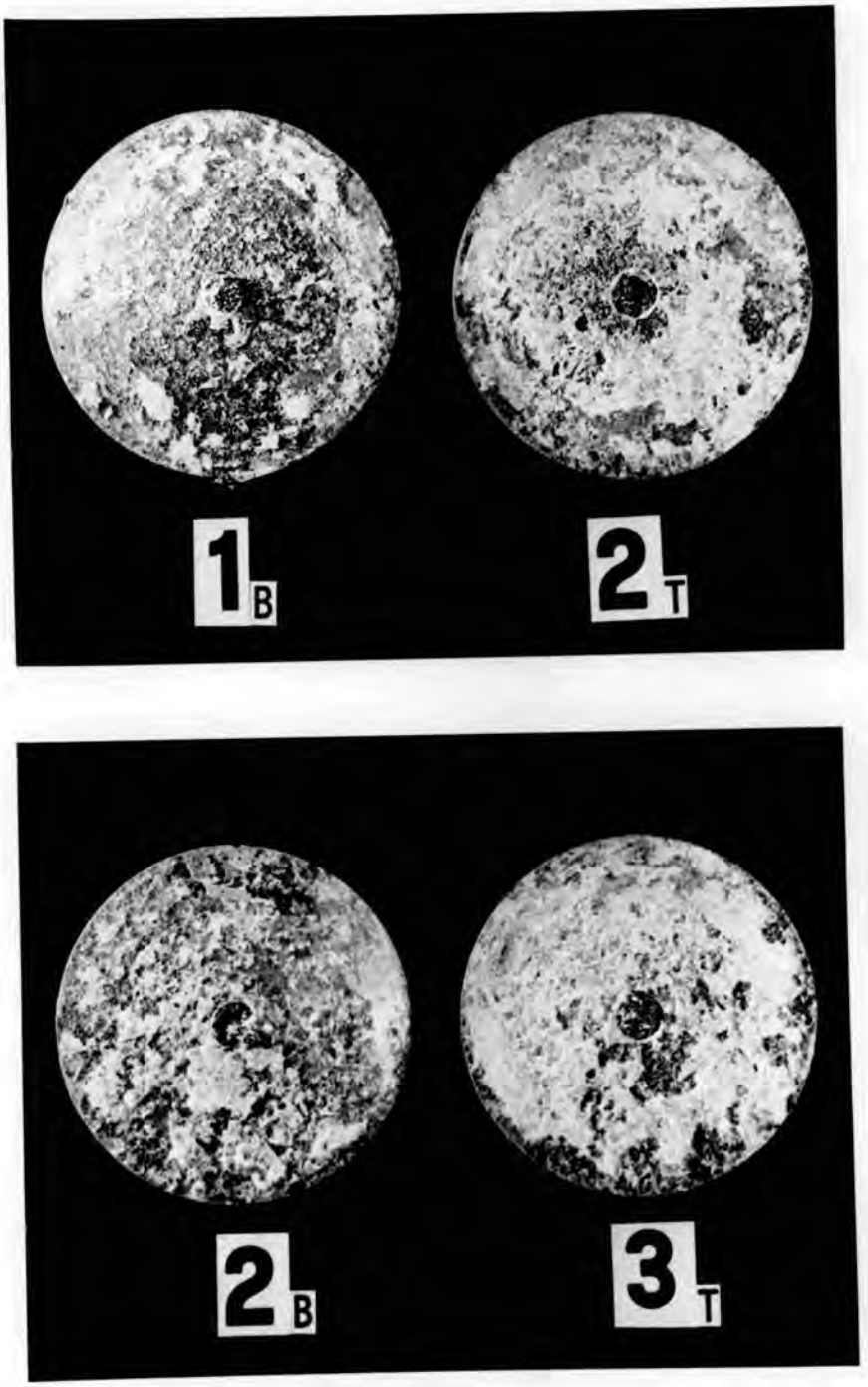

FIGURE 24. CORROSION PRODUCT DISTRIBUTION ON EXTRUDED BERYLLIUM INTERFACES AFTER 668 DAYS IN 0.005 M HYDROGEN PEROXIDE AT 85°C (T is top surface; B is bottom surface) ACTUAL SIZE

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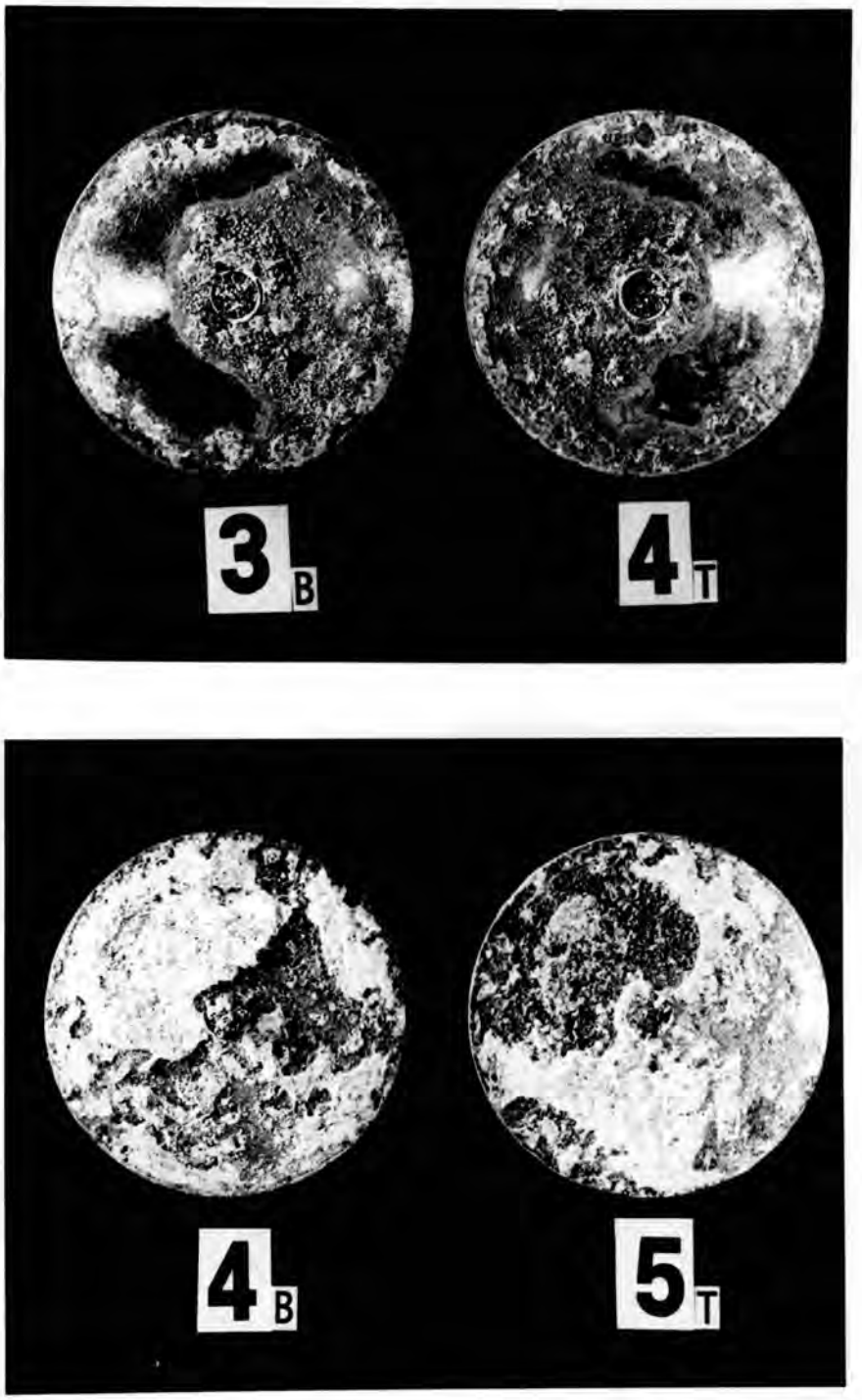

FIGURE 25. CORROSION PRODUCT DISTRIBUTION ON EXTRUDED BERYLLIUM INTERFACES AFTER 668 DAYS IN 0.005 M HYDROGEN PEROXIDE AT 85°C (T is top surface; B is bottom surface) ACTUAL SIZE

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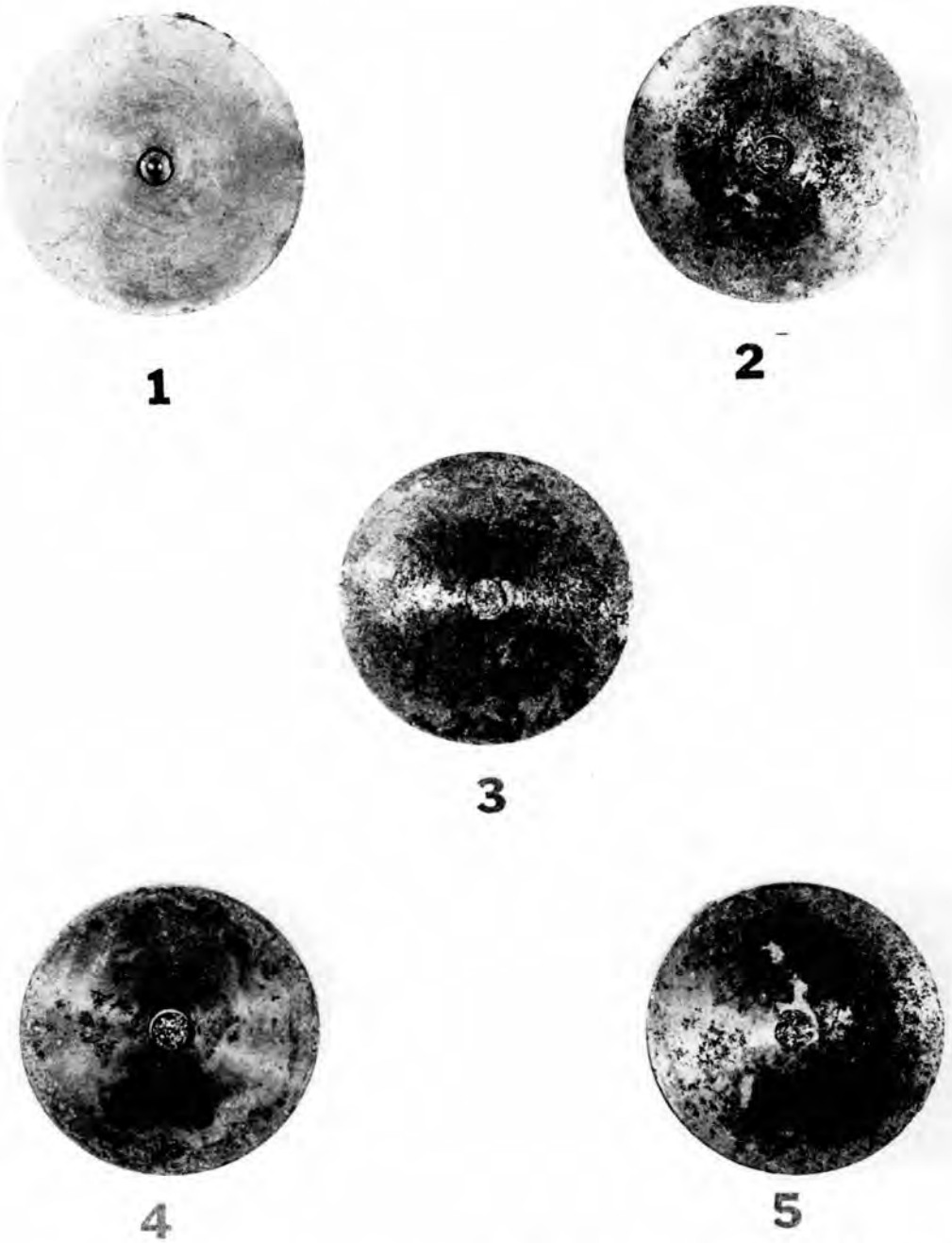

FIGURE 26. EXTRUDED BERYLLIUM SURFACES (after cleaning) SHOWING EXTENT OF LOCALIZED CORROSION ATTACK AFTER 668 DAYS IN 0.005 M HYDROGEN PEROXIDE AT 85°C. ACTUAL SIZE