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LUCAS HEIGHTS

STUDY OF THE VARIABLES AFFECTING THE CORROSION OF BERYLLIUM IN CARBON DIOXIDE

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ABSTRACT

Beryllium is a favoured canning and/or moderating material in the proposed Australian High Temperature Gas Cooled Reactor. With carbon dioxide as the most likely coolant a detailed knowledge of the corrosion of beryllium in this gas is required. Two separate investigations have proceeded simultaneously.

First the effect of the following variables was studied; surface preparation of the specimen, temperature (100–725 °C), pressure (0–280 p.s.i.g.), velocity, and impurity content of the gas. The influence of irradiation has not yet been studied. Autoclaves, thermobalances, and dynamic loops were used. The results were statistically analysed and kinetic data obtained. In all cases specimens with etched surfaces yielded approximately 25–30 per cent. greater weight gains than specimens with ground or polished surfaces. On extruded material no "breakaway" oxidation was encountered below 650 °C in commercially dry gas ($<$ 20 p.p.m. moisture). The rate of attack was to some extent affected by the pressure of the gas. Breakaway was only observed in one series of specimens at 650 °C. In this particular case the gas pressure was 280 p.s.i.g. However, it seems that surface temperatures of beryllium cans made from extruded material should be maintained below 650 °C in a reactor system using the commercially pure carbon dioxide as coolant.

In the second approach a more basic study of the chemistry of the reaction was made as well as a detailed investigation into the variation caused by differences in the composition and fabrication of the metal. Spiral spring balances at atmospheric pressure were used. Extruded material made from beryllium powder oxidized in dry oxygen for a short period of time had greatly enhanced oxidation resistance when exposed to carbon dioxide. Some of the material exposed to wet carbon dioxide at 700 °C and atmospheric pressure did not exhibit "breakaway" oxidation. The weight gains after 1,000 hours exposure under these conditions were never greater than 0.5 mg/cm^2.

Some comparisons were made between the reaction rates of beryllium with oxygen and carbon dioxide. In certain circumstances dry oxygen gave breakaway oxidation whereas carbon dioxide did not.

CONTENTS

FIGURES

(continued)

CONTENTS (continued)

1. INTRODUCTION

In the high–temperature gas–cooled reactor being developed by the Australian Atomic Energy Commission and in many other reactor systems at present being developed throughout the world, beryllium is envisaged as a moderator and/or canning material, while carbon dioxide is a favoured coolant. Thus the study of beryllium compatibility with carbon dioxide is being pursued actively by many workers. Published results show many discrepancies and these are considered to be due to lack of understanding of the many variables concerned.

Preliminary studies were made by Munro and Williams (1956) followed by Antill and Higgins (1960). Both these workers showed that, in the temperature range 650° to 750°C, two distinctly different types of attack could take place. In the first type the rate of attack decreased and it was suggested by Munro and Williams (1956) that some form of protective film was being formed on the surface of the metal. The second type, usually described as "breakaway" oxidation involved an accelerating reaction. This type was usually associated with the presence of water vapour in the carbon dioxide. This breakaway attack must be avoided in any use of beryllium in a reactor system.

Gregg, Hussey, and Jepson (1960) studied the chemistry of the reaction of beryllium with carbon dioxide in the temperature range 500 to 750°C, and showed that the following two reactions occur, the first being predominant

$$\mathrm{Be} + \mathrm{CO_2} = \mathrm{BeO} + \mathrm{CO}$$

$$\mathrm{2Be} + \mathrm{CO_2} = \mathrm{2BeO} + \mathrm{C.}$$

They also showed that small amounts of beryllium carbide were formed, most probably from the reaction of beryllium with deposited carbon.

All the work described above was carried out at pressures of 1 atmosphere or less. The aims of the work described in this paper involve a study of the effects of temperature; pressure, velocity, and composition of gas; and surface treatment of the specimens on the reaction of carbon dioxide with beryllium. The study of the effect of irradiation is also in progress but results are not given here.

2. EXPERIMENTAL METHODS

All the beryllium specimens were prepared from Pechiney powder by either extrusion or vacuum hot pressing techniques. Major impurities in the fabrication and their concentration limits are listed below:

O	0.28	–	1.9%
Cl	116	–	158 p.p.m.
Fe	312	–	690 p.p.m.
Al	281	–	763 p.p.m.
Si	23	–	452 p.p.m.
Ca	57	–	284 p.p.m.

The vacuum hot-pressed specimens were prepared at 600°C. However because of the lack of reproducibility in the results obtained from specimens prepared by this technique (see Section 3.1), the majority of samples were obtained from extrusions. Dimensions of the specimen discs varied from 0.5 to 1 inch in diameter and from 0.02 to 0.10 inch in thickness. These had been cut from rods which had been extruded directly from the powder (-100 mesh B.S.S.) at 1050°C with extrusion ratios between 10:1 and 16:1.

The carbon dioxide was supplied from a six-ton storage vessel and constant quality was maintained. This gas was produced by a fermentation process, and was of high commercial purity; the major contaminants were water vapour (< 20 p.p.m. v/v), oxygen (< 12 p.p.m. v/v), and nitrogen (50 p.p.m. v/v). Minor contaminants were sulphur dioxide (< 3 p.p.m.), oxides of nitrogen (< 1 p.p.m.) and various hydrocarbons and alcohols (< 1 p.p.m.).

The following variables were studied over the ranges stated:

temperature - 600 to 950°C

pressure - 0 to 280 p.s.i.g.

velocity - static to 200 f.p.s.

gas impurity content - water - 1 to 20,000 p.p.m.

In addition, three different surface preparations and their ultimate effect upon the corrosion were examined. In many of the semi-static tests at atmospheric pressure the specimens were chemically polished by immersion for 40 seconds at 110°C in a standard chromic-phosphoric acid bath. In other tests, the specimens were polished mechanically on 400 grade silicon carbide paper while in a third series of tests the specimens were exposed with ground or machined surfaces.

A variety of equipment was used in this work. Many of the tests at atmospheric pressure were done on a sensitive quartz spiral thermobalance. Figure 1 is a diagram of the thermobalance which is based on the principle of McBain and Bakr (1926). The beryllium sample A, contained in a quartz reaction vessel B is suspended by means of a fine platinum wire C from the quartz spring D. The extension of the spring and hence the weight of the sample is measured using a cathetometer. The quartz spring is contained in a water-jacketed glass envelope, around which thermostatted water (40°C ± 0.3°C) is continuously circulated. The sensitivity of this type of balance varied from ± 0.01 mg to ± 0.08 mg depending on the type of spring used.

Other tests at atmospheric pressure were carried out on a continuously-recording Stanton thermobalance which had an accuracy of ± 0.01 mg. Experiments at elevated pressures were performed using pressure vessels of the type shown in Figure 2. In the pressure vessel, temperature gradients of less than 5°C were obtained at all temperatures. At least sixteen replicate specimens were exposed in each vessel. Specimens were weighed at defined intervals of time, and experiments of up to 2,500 hours duration were completed. Water at 100 and 200 p.p.m. was introduced into the gas for some of these tests by passing a small portion of the gas stream through a bubbler in a thermostatically-controlled water bath. The effect of velocity was studied using the small dynamic loop previously described by Draycott and Smith (1960). These tests were of 100 hours duration.

Thermogravimetric data were supplemented by metallographic and X-ray analysis of the exposed specimens.

3. RESULTS

3.1 Materials Tested

Although most experiments were done with specimens cut from extruded rods, some initial tests were made on vacuum hot-pressed material. One series of specimens cut from a rod fabricated in this manner was exposed to commercially dry carbon dioxide at 625°C and 150 p.s.i.g.

The weight gain-time curves shown in Figure 3 have an extensive scatter with some specimens gaining up to 6 mg/cm^2 after 1100 hours exposure. Even so, the rate of weight gain was decelerating and suggested that breakaway conditions had not occurred. The behaviour of these vacuum hot-pressed specimens varied greatly. Much better reproducibility was obtained with specimens of extruded beryllium (see Figure 4 for weight gain data of extruded specimens exposed under same conditions) and all subsequent tests were carried out using this material.

3.2 Surface Treatment

The effect of surface treatment before exposure was studied in two series of experiments. The first series was carried out in pressure vessels using a range of temperature and pressure where only oxidation in the pre-breakaway stage occurred. The results are summarized in Figure 5. Each curve represents the mean of 8 specimens. In all cases, specimens with etched surfaces gained more weight than specimens with ground surfaces; while weight gains of specimens with mechanically polished surfaces were intermediate between these two. The greatest relative increase was obtained at 600 °C and 225 p.s.i.g. where specimens with etched surfaces had 68 per cent. greater weight gain than the specimens with ground surfaces.

Figure 6 shows weight gain-time curves from the second series of experiments for specimens with machined and etched surfaces exposed to wet carbon dioxide at 700 °C at 1 atmosphere in spiral spring thermobalances. Under these conditions breakaway occurred on both sets of specimens. However specimens with machined surfaces achieved weight gains of approximately 50 per cent. of those obtained by etched specimens. Some similar results have previously been reported by Smith (1960) who also noted that the time of onset of breakaway was decreased by etching. Smith attributed these effects to work hardening of the ground or machined surfaces. In both cases studied here, penetration along grain boundaries was evident.

3.3 Temperature and Pressure

Using the equipment shown in Figure 2 the temperature and pressure variables were studied over the temperature range 600 to 725 °C with pressures of 150, 225, and 280 p.s.i.g. Commercially dry gas was used in all these tests; the moisture content of the gas never exceeded 20 p.p.m., and was usually in the range 8 to 12 p.p.m. The minimum duration of each experiment was 1000 hours and in some cases extended up to 2500 hours.

Initially, reproducible results were difficult to obtain, and were mainly attributed to variations between extrusions and to some extent variations along an extruded rod. However, after duplication of some experiments and by testing a sufficiently large number of replicate specimens in each case, definite trends with pressure and temperature could be obtained from statistical analysis of the weight gain data.

Some of these experiments were done on specimens with etched and ground surfaces although the majority of tests used ground specimens only. Weight gain-time curves for specimens with ground surfaces exposed at a series of temperatures for each of the three pressures 150, 225, and 280 p.s.i.g. are shown in Figure 7. Each curve represents a mean of the weight gains recorded for at least sixteen specimens. The weight gains of 67 per cent. of the specimens fall within 10 per cent. of the curves drawn for experiments at 150 p.s.i.g., while 90 per cent. fall within 10 per cent of the curves at the other two pressures.

The weight gains of the specimens exposed at all temperatures at a pressure of 150 p.s.i.g. are small, and suggest that breakaway oxidation would be most unlikely under these conditions. The variation of weight gain with temperature was small but well defined. However some overlapping occurred, particularly in the temperature range 650 to 700 °C. In all cases the rate of attack decelerated and suggested the formation of some variety of protective film on the surface of the metal. However, metallographic examination showed that some large holes were present in some specimens which had been exposed at 650 °C and 150 p.s.i.g.; a section of one such specimen is reproduced in Figure 8. The mechanism of the formation of these holes is not clear at present although they were only observed in specimens from particular extrusions and may therefore be the result of peculiarities in fabrication.

Under a gas pressure of 225 p.s.i.g. all specimens gained more weight than specimens exposed at the same temperatures under a pressure of 150 p.s.i.g. Again no breakaway oxidation occurred in any specimens with ground surfaces. However out of eight specimens with etched surfaces exposed at 700 °C and 225 p.s.i.g. breakaway occurred on a few specimens after periods of exposure varying from 500 to 900 hours. The weight gain–time curves for the individual specimens exposed under these conditions are shown in Figure 9. A photomicrograph of one of these specimens is shown in Figure 10, and reveals how breakaway oxidation was accompanied by intergranular penetration along paths which lie roughly parallel to the axis of extrusion.

At a gas pressure of 280 p.s.i.g. the rate of attack decelerated to some extent at 625 °C but this rate was greater and weight gain much higher than had been measured at pressures of 150 and 225 p.s.i.g. Breakaway oxidation did not occur at 625 °C in tests of 1000 hours duration. At both 650 °C and 675 °C and a gas pressure of 280 p.s.i.g. breakaway readily occurred: weight gains of up to 4.5 mg/cm^2 were obtained at 650 °C after 1000 hours exposure. Breakaway oxidation is associated with marked intergranular penetration; this penetration is shown in the photomicrograph of Figure 11. Some variations in weight gain of individual specimens were obtained under these conditions, as shown in Figure 12. After breakaway had occurred, the rate of attack did not continually accelerate but was rather less than linear. At 675 °C and 280 p.s.i.g. breakaway was again encountered but individual weight gains were less than were obtained at 650 °C and the same pressure. The curves for weight gains of individual specimens are shown in Figure 13. The rate of attack on these specimens apparently shows alternating accelerating and decelerating periods but overall the deviation from the linear is slight.

From these experiments it is clear that beryllium cannot be used as a cladding or moderating material in a carbon dioxide cooled reactor at temperatures of 650 °C and above, if the gas pressure exceeds 280 p.s.i.g. and the gas contains between 10 and 20 p.p.m. H_2O. The much greater attack which is encountered at the higher pressures may be due to the increased partial pressure of the water vapour rather than to the effect of the absolute gas pressure itself. This possibility is considered in a later section.

In beryllium, breakaway oxidation is accompanied by reaction in an irregular manner in the interior of the metal. Some depths of heavy attack have been measured microscopically on the specimens exposed at 650 °C and 280 p.s.i.g. These depths varied in one specimen from 2.0 to 8.0×10^{-3} inches with an average depth of 4.275×10^{-3} inches. The possible life of the material cannot therefore be estimated simply by measuring depths of penetration and by extrapolating rate data to longer periods.

3.4 Impurities in the Gas

Water vapour and oxygen are two major impurities in commercial carbon dioxide. A study was made of some reactions with extruded beryllium involving these gases. Five systems were examined, viz:

1. Dry carbon dioxide (O_2, $H_2O < 1$ p.p.m. v/v)
2. Carbon dioxide containing 100 p.p.m. v/v and 200 p.p.m. v/v water vapour, at 150 p.s.i.g. and 250 p.s.i.g.
3. Wet carbon dioxide, i.e. gas saturated with water vapour at ambient temperature (H_2O about 20,000 p.p.m. v/v)
4. Dry oxygen ($H_2O < 1$ p.p.m. v/v
5. Wet oxygen (H_2O about 20,000 p.p.m. v/v)

The reaction of beryllium with pure water vapour has been studied by other workers (Aylmore, Gregg and Jepson 1961; O'Connor and Roman, private communication).

Systems 1, 2, 4, and 5 were studied at one atmosphere pressure. Traces of oxygen were removed from carbon dioxide using reduced pyrolusite, while the dry gas was obtained by passage through a bed of Linde Molecular Sieves Type 5A.

These reactions were examined in the temperature range 650 to 900 °C, but the effect of temperature was not studied systematically. The experiments were designed rather to compare by thermogravimetric measurements the different rates of reaction with various gases, and to examine the respective products of reaction.

3.4.1 Reaction in dry carbon dioxide

Curves of weight gain versus time in Figure 14 describe the reaction of beryllium in dry carbon dioxide at various temperatures in the range 750 to 900 °C. The rates of reaction at all these temperatures, decreased with time. Some specimens were exposed at 800 °C for periods up to 4000 hours, and the results of these long-term tests are shown in Figure 15.

Thermogravimetric data suggest that at one atmosphere the reaction in dry carbon dioxide is "protective". That is, a surface film is formed which inhibits further reaction. In general this concept was supported by metallographic examination of corroded specimens: in most specimens there was no evidence of intergranular penetration or internal corrosion. However some specimens from particular batches of extruded beryllium, contained large cavities which were distributed throughout the interior of a specimen. This cavitation is shown in the photomicrograph given in Figure 16. The white areas represent beryllium metal and the large dark patches are empty cavities. These cavities were evidently formed during exposure to carbon dioxide: they were not present in the as-received metal, and they were not present in control specimens which had been heated in argon. Nevertheless it is not clear how these cavities originated. Since they were observed in specimens obtained from particular extrusions, they may arise from some unknown variable in the fabrication technique.

3.4.2 Reaction in carbon dioxide containing 100-200 p.p.m. v/v water vapour

Some experiments have been completed at 625 °C and pressures of 150 p.s.i.g. and 250 p.s.i.g., in which carbon dioxide containing 100 and 200 p.p.m. v/v water vapour has been used as a corrosive medium. The weight gains of beryllium specimens exposed under these conditions are plotted in Figure 17 as a function of time. At a pressure of 250 p.s.i.g., breakaway oxidation occurred. In the gas containing 200 p.p.m. v/v water vapour, breakaway oxidation began after about 150 to 250 hours, whilst in the gas containing 100 p.p.m. v/v, breakaway did not begin until after 500 hours.

3.4.3 Reaction in wet carbon dioxide

Figures 14 and 15 compare thermogravimetric data for the reaction in both dry and wet carbon dioxide. At temperatures above 640 °C, the reaction in wet carbon dioxide resulted in high weight gains after a short time, and breakaway oxidation occurred from the start. During the reaction, specimens distorted and swelled visibly. Surface cracks formed on each specimen (Figure 18).

Figure 19(d) shows the distribution of corrosion products in beryllium after exposure at 700 °C. Although a surface layer was formed for the most part corrosion was internal. The black areas represent beryllium oxide. There is also present an unidentified phase which was first observdd by Smith (1960); this phase is shown as light-grey patches which frequently appear interposed between beryllium oxide and unreacted beryllium metal.

X-ray diffraction measurements of corroded beryllium gave evidence that beryllium oxide and only trace amounts of beryllium carbide were formed during the reaction with wet carbon dioxide (Smith et al. 1961). The unidentified phase is present in appreciable quantity, and it is therefore unlikely to be beryllium carbide.

Although thermogravimetric data were consistent for different batches of extruded material, the distribution of corrosion products varied quite markedly from batch to batch. In general, intergranular penetration took place in two ways. In some specimens, penetration occurred along specific paths parallel to the axis of extrusion, and complete interpenetration occurred at an early stage of the breakaway process. Figures 19(a), (b), and (c) form a series of photomicrographs which show this type of distribution after different periods of exposure to wet carbon dioxide at 700 °C. In another series of specimens, however, penetration took place uniformly from the surface along a fairly well-defined reaction "front"; and regions in the centre of a specimen were relatively unaffected by corrosion (Figure 19(e)).

3.4.4 Reaction in both dry and wet oxygen

Figure 20 shows how two samples of beryllium reacted in dry oxygen at 750 °C and 800 °C respectively. Initially beryllium experienced a small but rapid gain in weight. Subsequently the reaction slowed down for a time, and then accelerated rapidly. A number of specimens obtained from different extrusions, all behaved in this manner when heated in oxygen.

At 800 °C the beryllium specimen disintegrated completely after 80 hours, although the weight gain was then only about 2 mg/cm^2. At 750 °C the final weight gain was 1.6 mg/cm2 after 100 hours exposure. At this temperature the sample which was about 0.5 mm thick, had deformed into a saucer-like shape; the surface was extensively cracked (Figure 21) and the diameter of the disc had increased by 10 per cent. The corroded specimen was fragile and broke easily at a touch.

Figure 22 shows a cross section of the specimen which had reacted at 750 °C. Inclusions of beryllium oxide were present, but for the most part the specimen was interpenetrated by large, elongated cavities. Some of these cavities have been filled by plastic mounting-material during metallographic preparation.

Corrosion by both wet and dry oxygen have the same general features. Figure 23 contains thermogravimetric curves which describe the reaction in wet oxygen at 650 °C, 700 °C, and 750 °C. The presence of water increases rates of reaction but the general shape of each curve is the same. Again, in wet oxygen, the volume of beryllium samples increased and each specimen was interpenetrated by large cavities.

The cavities were apparently formed during and as a result of reaction. We denote the observed increase in volume of a specimen by ΔV^{I}. This quantity was calculated for three samples, by accurately measuring dimensions before and after reaction. ΔV^{I} was then compared with ΔV^{II}, where ΔV^{II} is the change in volume due to the formation of beryllium oxide. In the calculation of ΔV^{II}, it was assumed that the entire weight change of a beryllium sample arose from the formation of beryllium oxide. It was also assumed that the density of beryllium was 1.98 g/cm^3 and the density of beryllium oxide was 3.01 g/cm3.

Table 1 lists values of both ΔV^{I} and ΔV^{II} computed for three specimens.

TABLE 1

Specimen No.	Gas Composition	Weight Change mg	Temp. of Reaction	ΔV^{II} cm3	ΔV^{I} cm3	$\frac{\Delta V^{I}}{\Delta V^{II}}$
41	Wet CO_2	46.8	700	1.07×10^{-2}	1.14×10^{-2}	1.07
37	Wet O_2	0.19	650	4.33×10^{-5}	3.14×10^{-4}	1.38×10
47	Wet O_2	3.28	700	7.51×10^{-4}	7.51×10^{-4}	3.85×10^{2}

The expansion of specimen 41 can be accounted for by the change in volume which accompanies the conversion of beryllium to beryllium oxide. Thus during reaction in wet carbon dioxide no large cavities are formed. By contrast, sample 37 expanded about 10 times the expected amount; similarly the change in volume of sample 47 was 100 times the change in volume due to formation of beryllium oxide.

This unexpectedly high increase in volume during reaction with wet oxygen suggests very strongly that large empty cavities are formed as corrosion takes place.

The unidentified phase which was formed in wet carbon dioxide, was not present in beryllium which had corroded in dry oxygen or in wet oxygen.

3.5 Velocity

The weight gains of beryllium specimens have been measured after exposure to commercially pure carbon dioxide at 625, 650, 675 °C and at velocities of 100, 150, and 200 ft/sec respectively. The pressure in all these tests was slightly above atmospheric. All tests were of 100 hours duration. The results listed in Table 2 show that the weight gains measured in these tests were somewhat lower than weight gains measured in semi-static systems at the same temperatures but at higher pressures. Breakaway was not encountered. At present it appears that the velocity of the gas has little effect upon the corrosion of beryllium in carbon dioxide although at the higher temperatures slightly greater weight gains were encountered at the higher velocities.

TABLE 2

Temperature	Weight Gain mg/cm^2		
	100 ft/sec	150 ft/sec	200 ft/sec
625	0.052	0.033	–
650	0.023	0.048	0.046
675	–	0.041	0.066

3.6 Material Variable

Smith (1960) reported that beryllium which had a high oxide content was more resistant to corrosion than the purer material when these were heated in wet carbon dioxide. This observation was confirmed by more extended studies which are reported in detail elsewhere (Smith et al. 1961) but because of the apparent value of this technique and the assistance these results offer in the general interpretation of the mechanism of attack they are reproduced here.

The beryllium specimens used in these tests were heated at 700 ° C and 800 °C in wet carbon dioxide for varying periods of time on a quartz spring thermobalance. These specimens were cut from extruded rods or rolled sheets. Beryllium powder was oxidized in dry oxygen at 800 °C for periods up to two hours before extrusion or rolling. This resulted in a material containing up to 2 per cent. oxygen.

The results of the exposure tests are summarized in Table 3. In both extruded and rolled materials the specimens prepared from oxidized powder were markedly resistant to corrosion.

TABLE 3

RESULTS OF CORROSION TESTS CARRIED OUT ON VARIOUS TYPES OF BERYLLIUM USING WET CARBON DIOXIDE AT 700 °C AND 800 °C

Type of Beryllium	Duration of Test Hours	Final Weight Gain mg/cm^2	BeO Content wt.%	Temp. of Reaction °C
Clean extruded Be	168	9.7	0.3	700
	112	10.2	0.3	700
	94	10.1	0.3	700
Extruded Be powder oxidized for 2 hours at 800 °C	840	0.82	1.5–2.0	700
Clean Be sheet	97	1.75	0.3	700
	141	6.09	0.3	700
Be sheet from powder oxidized for ½ hour at 800 °C	1176	0.29	1.5–2.0	700
	1513	0.34		800
	957	0.25		700
Be sheet from powder oxidized for 2 hours	3820	0.32	1.5–2.0	700

These results confirm the earlier reports of Smith (1960), but much more detailed study is required before this material can be accepted for beryllium in a reactor-system. However, an alternative to the provision and maintenance of a completely dry gas in the reactor circuit is now available.

3.7 Summary of Results

(1) In commercially pure carbon dioxide (10–20 p.p.m. v/v H_2O), breakaway oxidation of extruded beryllium does not take place in periods up to 1500 hours at temperatures up to 650 °C, if the gas pressure is less than 280 p.s.i.g.

(2) If 100 p.p.m. v/v of water vapour is added to carbon dioxide, then breakaway readily takes place at 625 °C and 250 p.s.i.g.

(3) In wet carbon dioxide (about 20,000 p.p.m. v/v H_2O) at one atmosphere, breakaway oxidation is observed at all temperatures in the range 640 to 900 °C. By contrast, the reaction with completely dry carbon dioxide is protective for at least 4000 hours at 800 °C.

(4) Breakaway oxidation is particularly marked in the reaction with both wet and dry oxygen at temperatures above 700 °C.

(5) Breakaway oxidation in wet carbon dioxide, wet oxygen and dry oxygen is an internal, intergranular process, which is always accompanied by visible swelling and sometimes final disintegration of beryllium specimens.

(6) Two major products of the reaction with wet carbon dioxide are beryllium oxide and an unidentified phase. This phase is not formed in the reaction with pure water vapour (O'Connor and Roman, private communication), dry oxygen, or wet oxygen; it is not beryllium carbide but is possibly some modified form of the oxide.

3.8 Discussion

This work has shown that at temperatures up to 650 °C, beryllium which has been prepared by extrusion can be resistant to corrosion by commercially-pure carbon dioxide at pressures up to 280 p.s.i.g. At higher pressures and temperatures, however, breakaway oxidation occurs. In spite of the wide variation in behaviour of individual samples these limits of temperature and pressure have been defined for carbon dioxide which contains about 20 p.p.m. v/v water-vapour and 20 p.p.m. v/v oxygen.

However, rates of reaction and the initiation of breakaway oxidation are modified by quite small amounts of gaseous impurities. Corrosion of beryllium in carbon dioxide is particularly affected by the presence of moisture. Thus at 625 °C and 250 p.s.i.g., breakaway oxidation occurs if carbon dioxide contains 100 p.p.m. v/v water-vapour, whereas the reaction is protective in commercially dry gas under the same conditions of temperature and pressure.

Aylmore, Gregg, and Jepson (1961) showed that the rate of reaction of beryllium in pure water vapour at 700 °C was sensitive to the pressure. At a pressure of 5×10^{-4} mm Hg, the reaction was slow and decelerating; but when the pressure was increased to 0.48 mg Hg, then breakaway oxidation took place.

It appears then, that the corrosion of beryllium in carbon dioxide is related, not to the moisture content but to the partial pressure of water vapour. This effect would account for the apparent influence of gas pressure on the corrosion of beryllium. If we assume that the commercial carbon dioxide contained 20 p.p.m. v/v moisture, then at atmospheric pressure this would involve a partial pressure of about 1.5×10^{-2} mm Hg; at 280 p.s.i.g. the corresponding partial pressure is about 2.8×10^{-1} mm Hg. On this basis a reactor system involving carbon dioxide at high pressure and beryllium of the type studied here would require extremely rigorous control of moisture content and probably oxygen content also.

A promising approach to the problem of gas compatibility of beryllium, involves the study of breakaway oxidation, its mechanism, and the factors which inhibit it. Breakaway oxidation of beryllium has been observed for the reaction in carbon dioxide containing more than 20 p.p.m. v/v moisture and in oxygen in both the dry ($<$ 2 p.p.m. v/v H_2O) and wet state. This type of oxidation is associated with considerable intergranular penetration, and visible swelling of beryllium specimens. Swelling of beryllium must be accompanied by stress and rearrangement at grain boundaries, and possibly intergranular cracking. In this way fresh reactive surfaces are continuously exposed. This process may partly account for the accelerating rates of reaction which are involved during breakaway.

It is not yet clear how the breakaway oxidation is initiated or why subsequent corrosion should take place along preferred paths in the interior of the metal. However it is clear that breakaway oxidation of beryllium is an intergranular effect and that to inhibit it an appropriate modification of the grain-boundary condition is required. In this respect the work of Smith et al. (1961) shows that breakaway conditions may be avoided if beryllium oxide is present as fine intergranular precipitates.

The use of beryllium in carbon dioxide cooled reactors at temperatures higher than once considered possible may now be achieved by modification of the material before fabrication, as well as by stringent control of the moisture level in a coolant circuit.

4. ACKNOWLEDGMENTS

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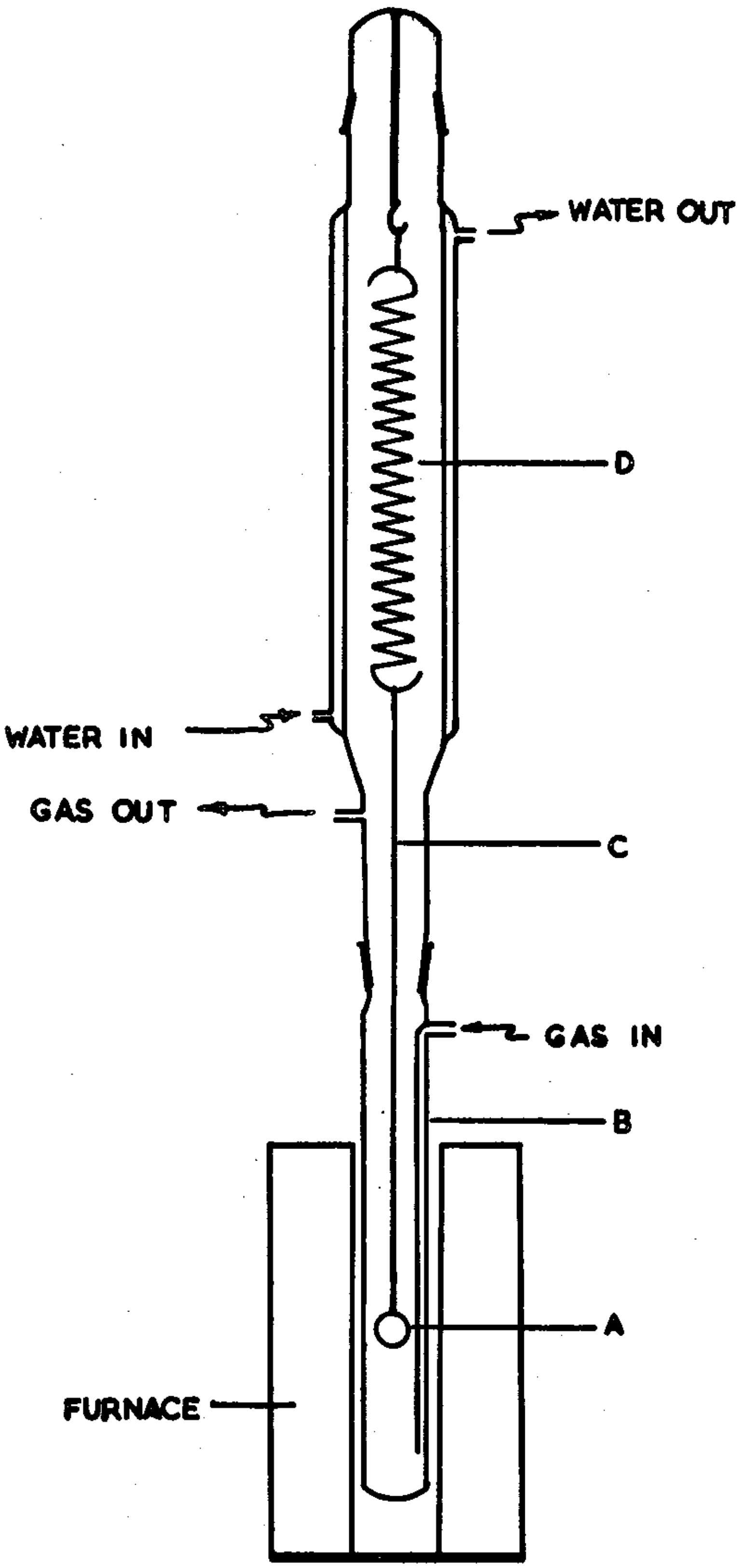


QUARTZ SPRING THERMOBALANCE

FIGURE 1

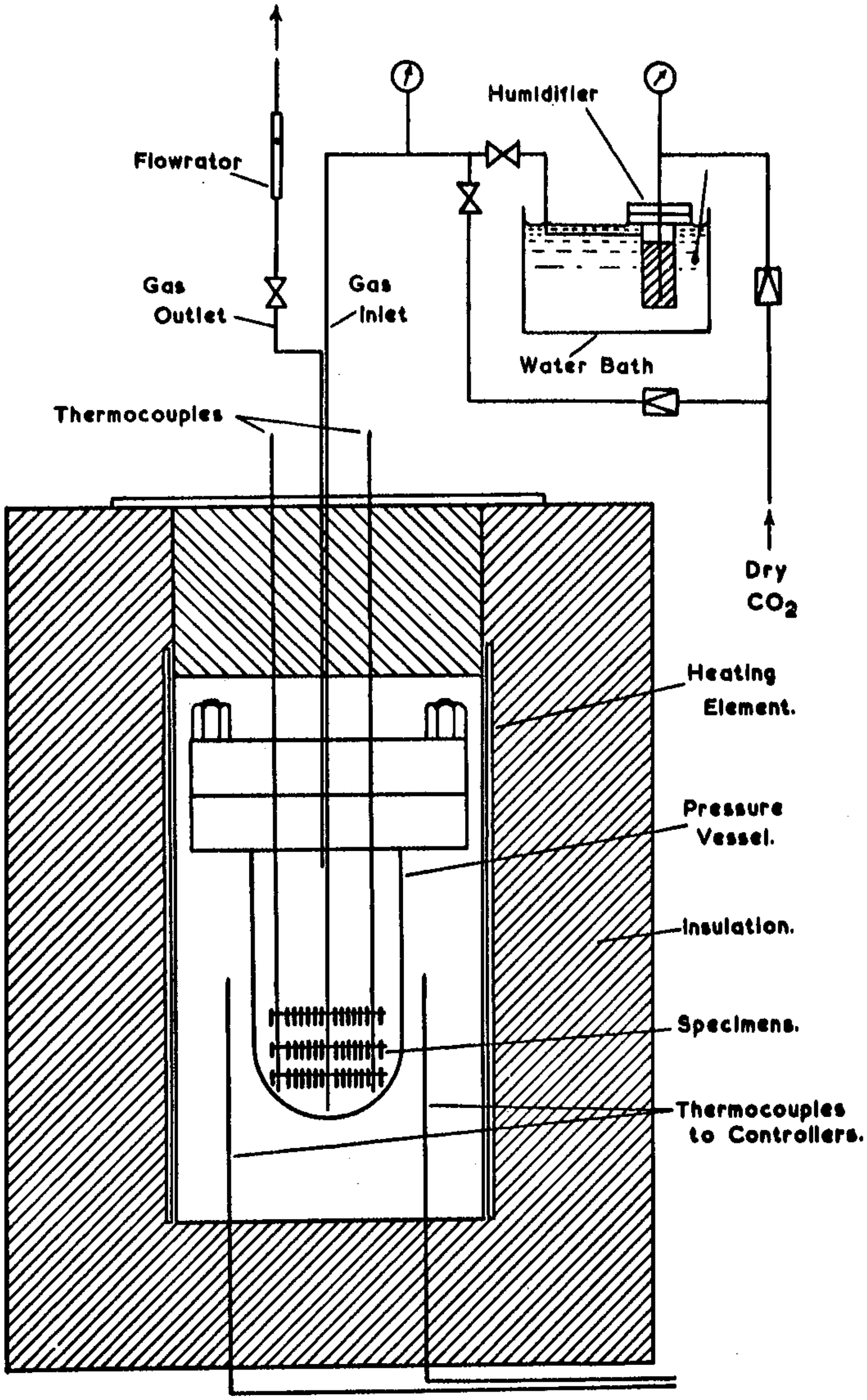


FIG. 2. G.E.C. UNITS SHOWING THE APPARATUS USED TO CONTROL MOISTURE.

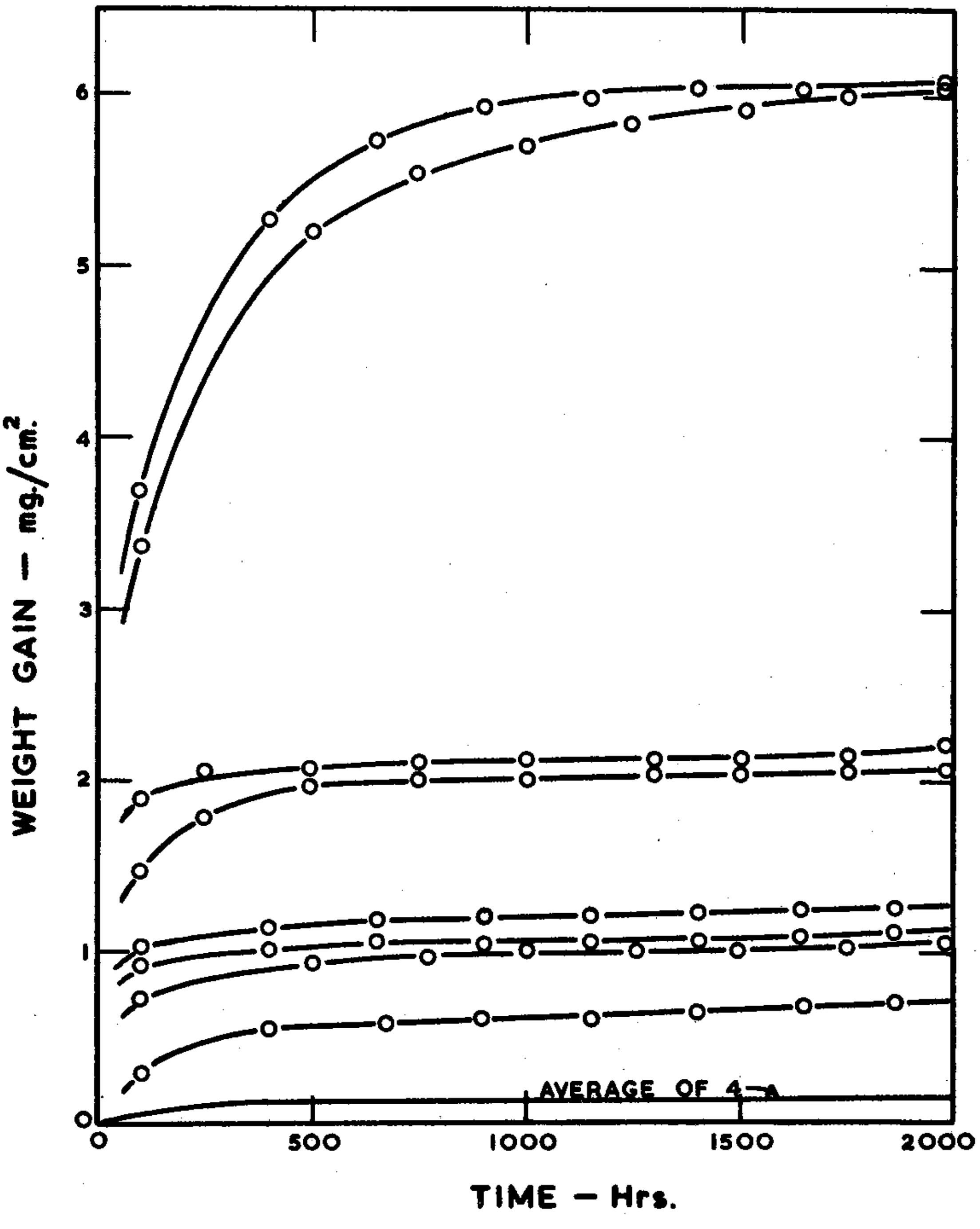


FIG. 3. WEIGHT GAIN OF INDIVIDUAL SAMPLES OF VACUUM HOT PRESSED Be AT 625°C & 150 p.s.i.g.

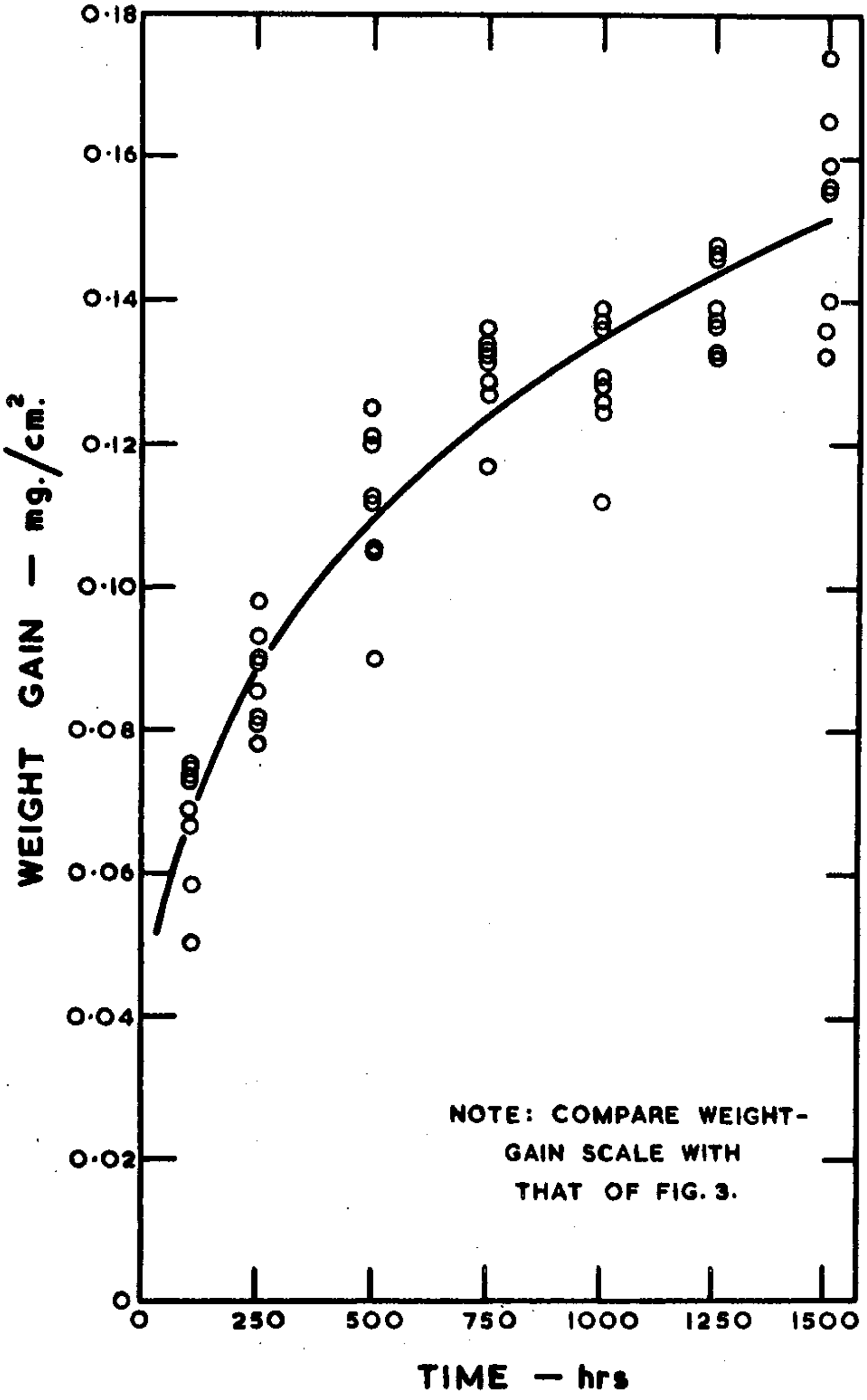


FIG. 4. WEIGHT GAIN OF INDIVIDUAL SAMPLES OF EXTRUDED Be AT 625°C & 150 p.s.i.g.

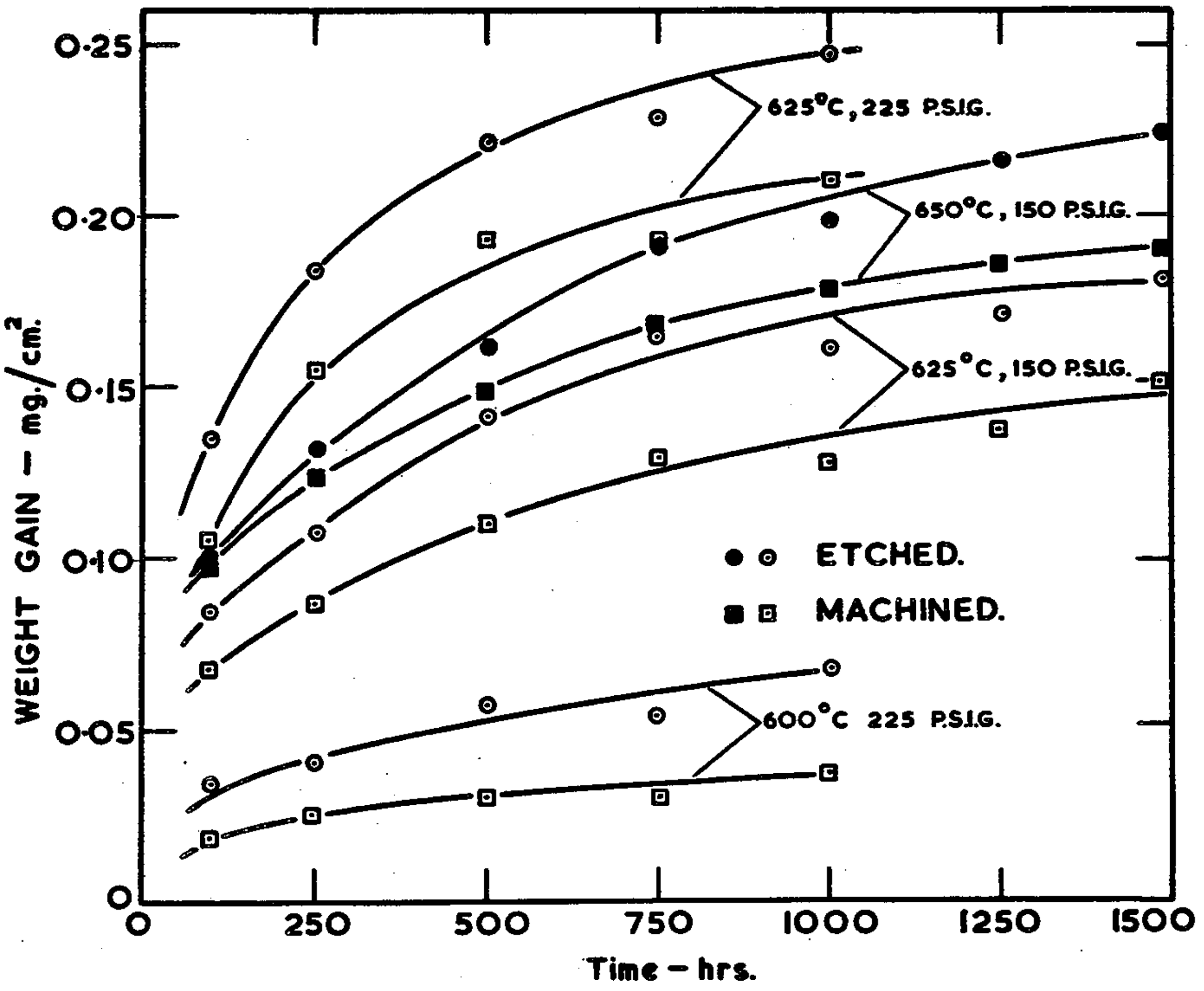
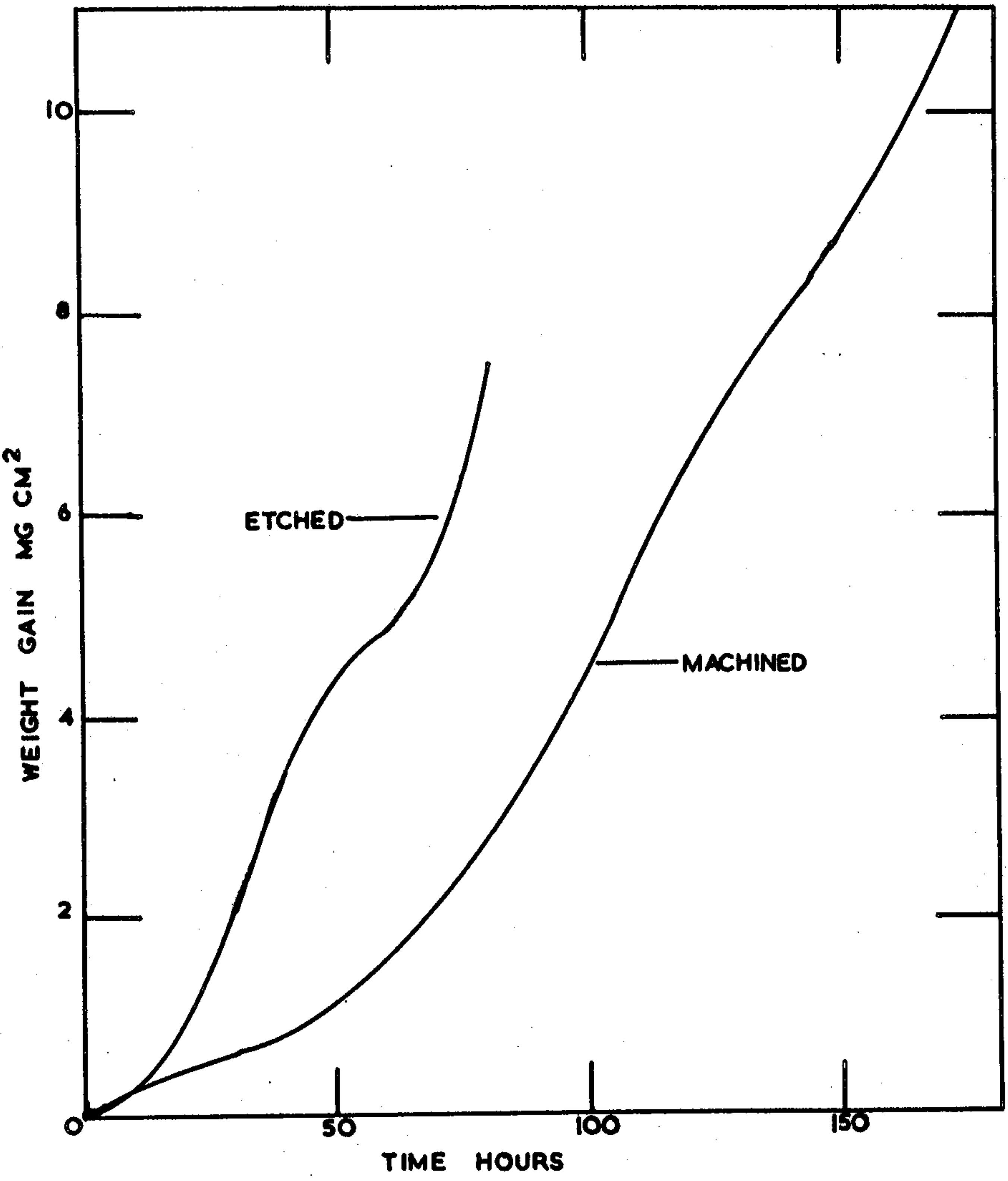


FIG. 5. THE EFFECT OF SURFACE TREATMENT ON THE WEIGHT GAIN OF Be SPECIMENS EXPOSED TO CO_2.



REACTION OF BERYLLIUM IN WET CARBON DIOXIDE AT 700°C
EFFECT OF SURFACE TREATMENT

FIGURE 6

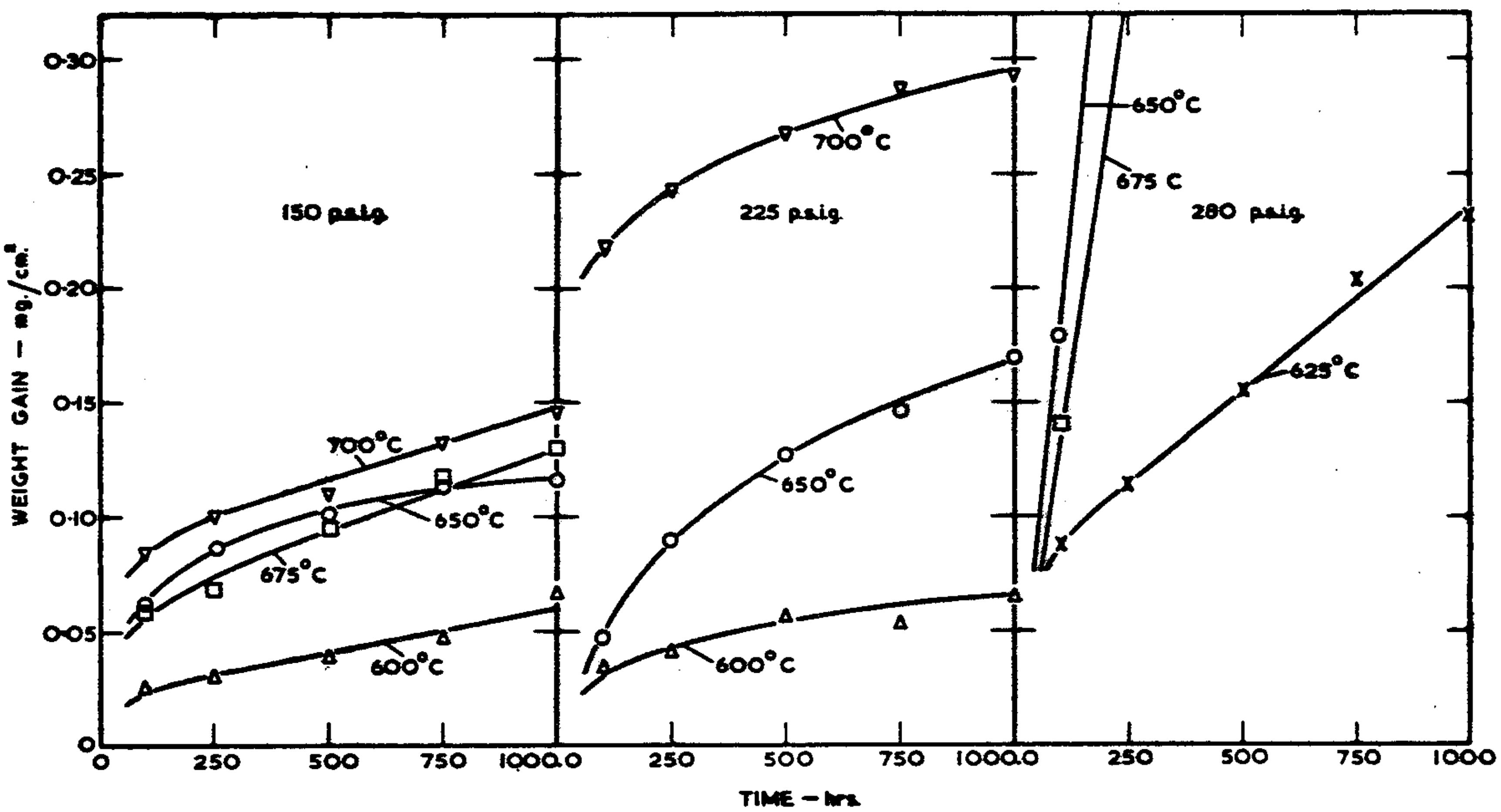


FIG. 7 VARIATION OF WEIGHT GAIN OF Be SPECIMENS IN CO_2 WITH TEMPERATURE & PRESSURE.

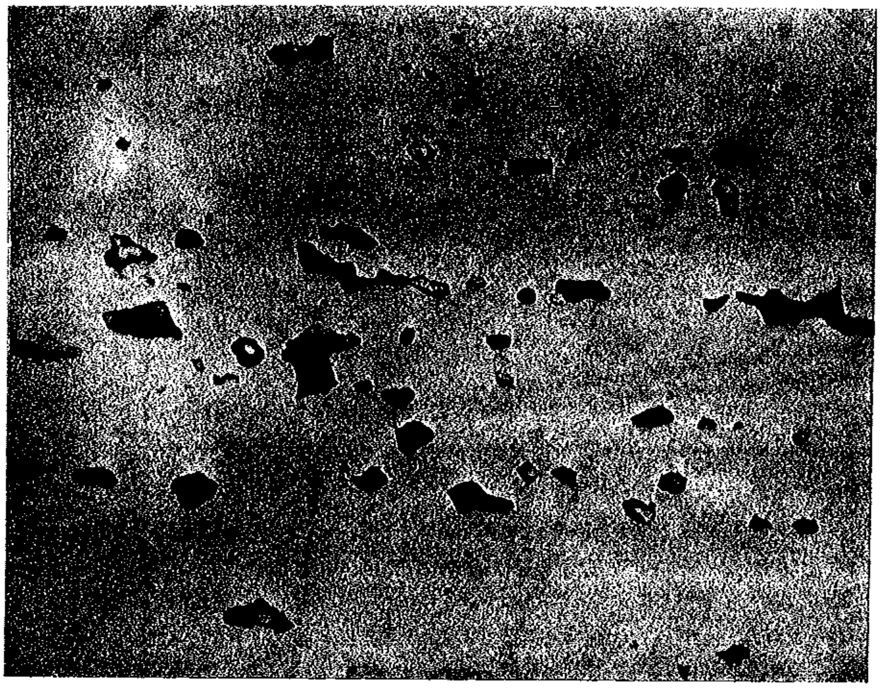


FIGURE 8 BERYLLIUM AFTER EXPOSURE TO COMMERCIALLY DRY CARBON DIOXIDE AT 650 °C AND 250 p.s.i.g. X 500

Weight Gain: 0.057 mg/cm^2 after 1000 hours

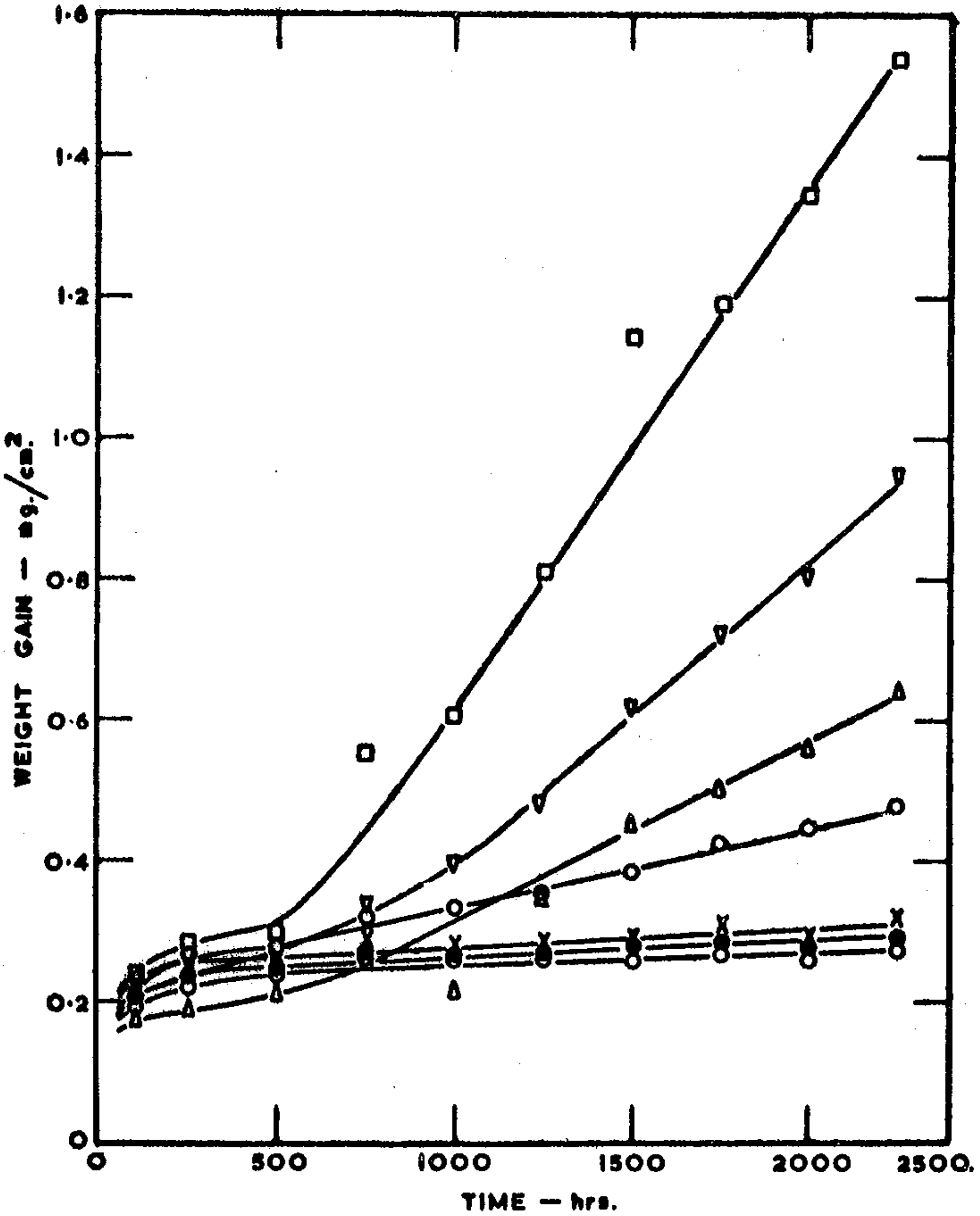


FIG. 9 WEIGHT GAIN – TIME CURVES FOR INDIVIDUAL ETCHED Be SPECIMENS IN CO_2 AT 700°C & 225 p.s.i.g.

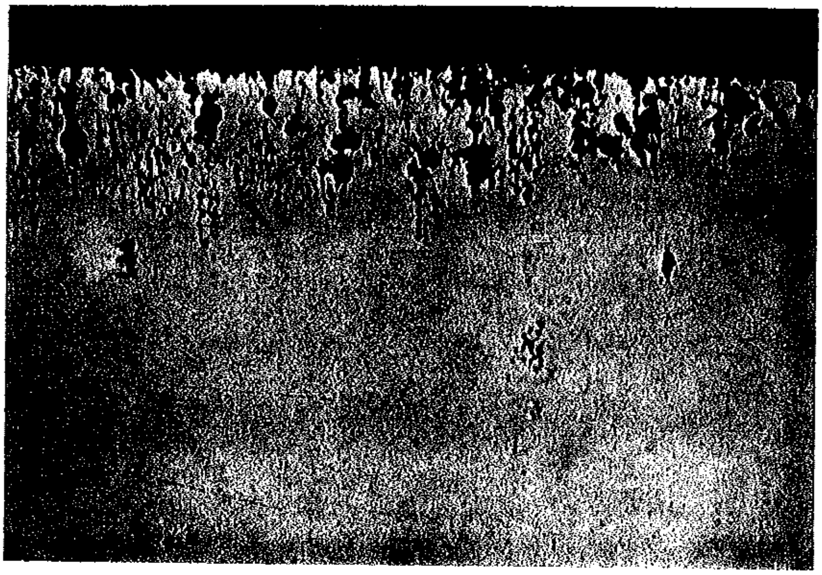


FIGURE 10 BERYLLIUM AFTER EXPOSURE TO COMMERCIALLY DRY CARBON DIOXIDE AT 700 °C AND 225 p.s.i.g. X 75

Weight Gain: 1.54 mg/cm^2 after 700 hours

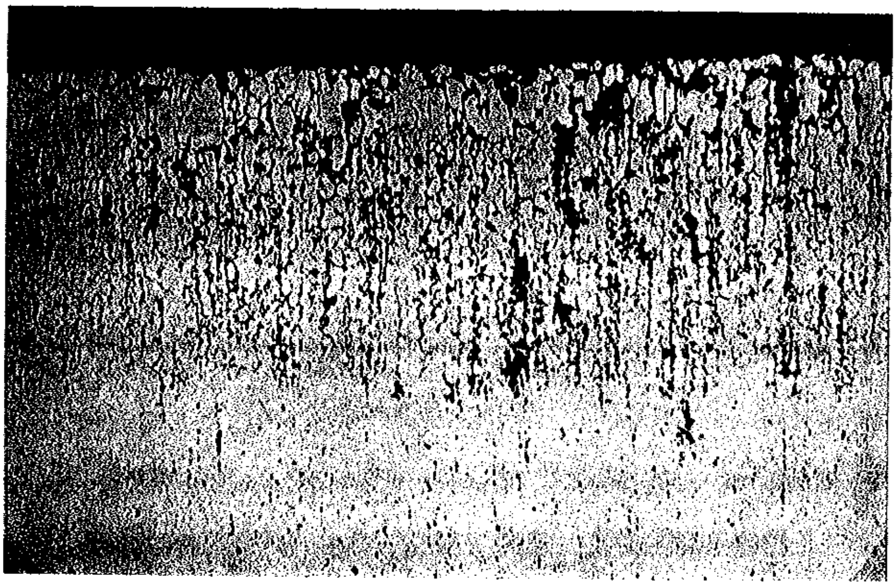


FIGURE 11 BERYLLIUM AFTER EXPOSURE TO COMMERCIALLY DRY CARBON DIOXIDE AT 650 °C AND 280 p.s.i.g. X 75

Weight Gain: 3.08 mg/cm^2 after 1000 hours

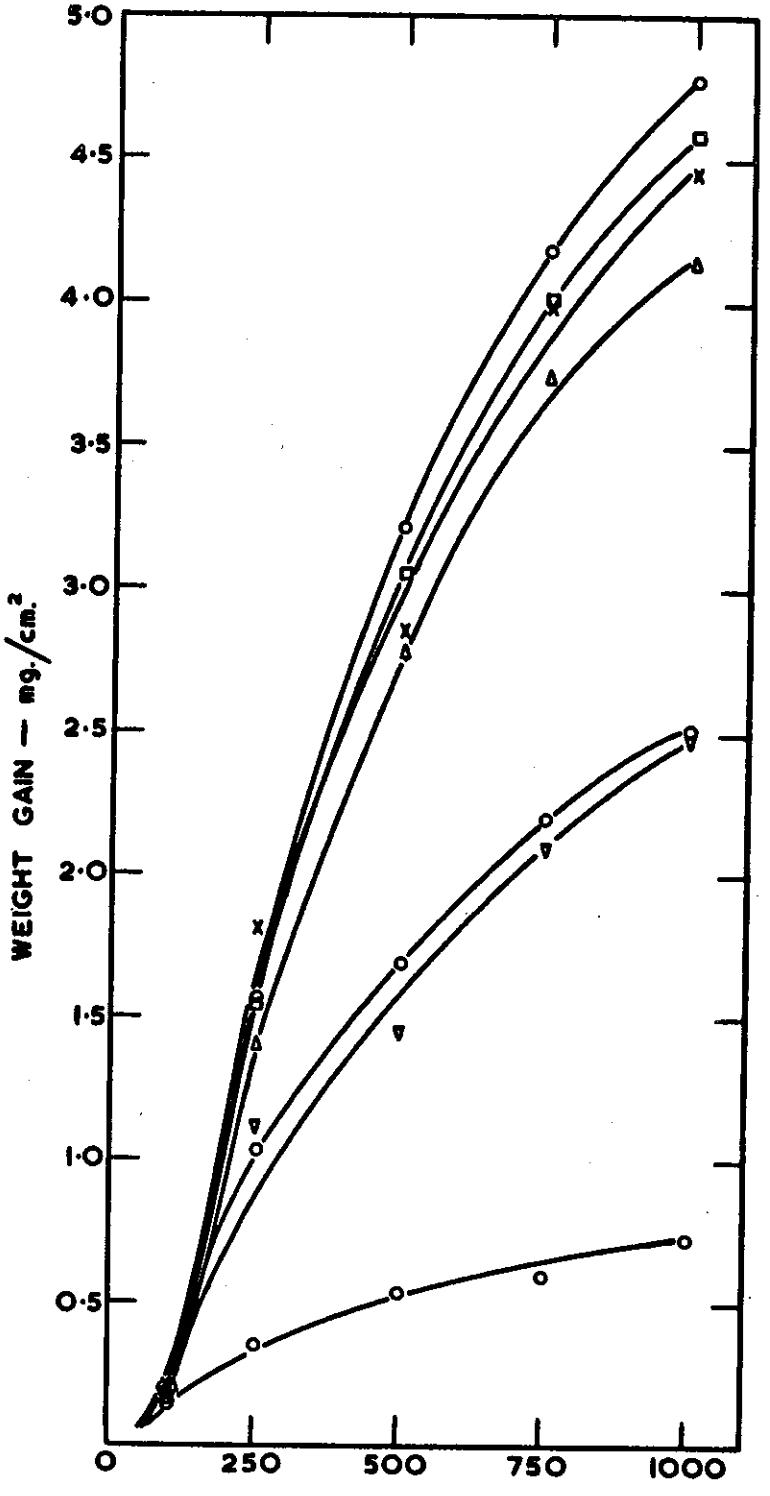


FIG 12 WEIGHT GAIN — TIME CURVES FOR INDIVIDUAL Be SPECIMENS IN CO_2 AT 650°C & 280 p.s.i.g.

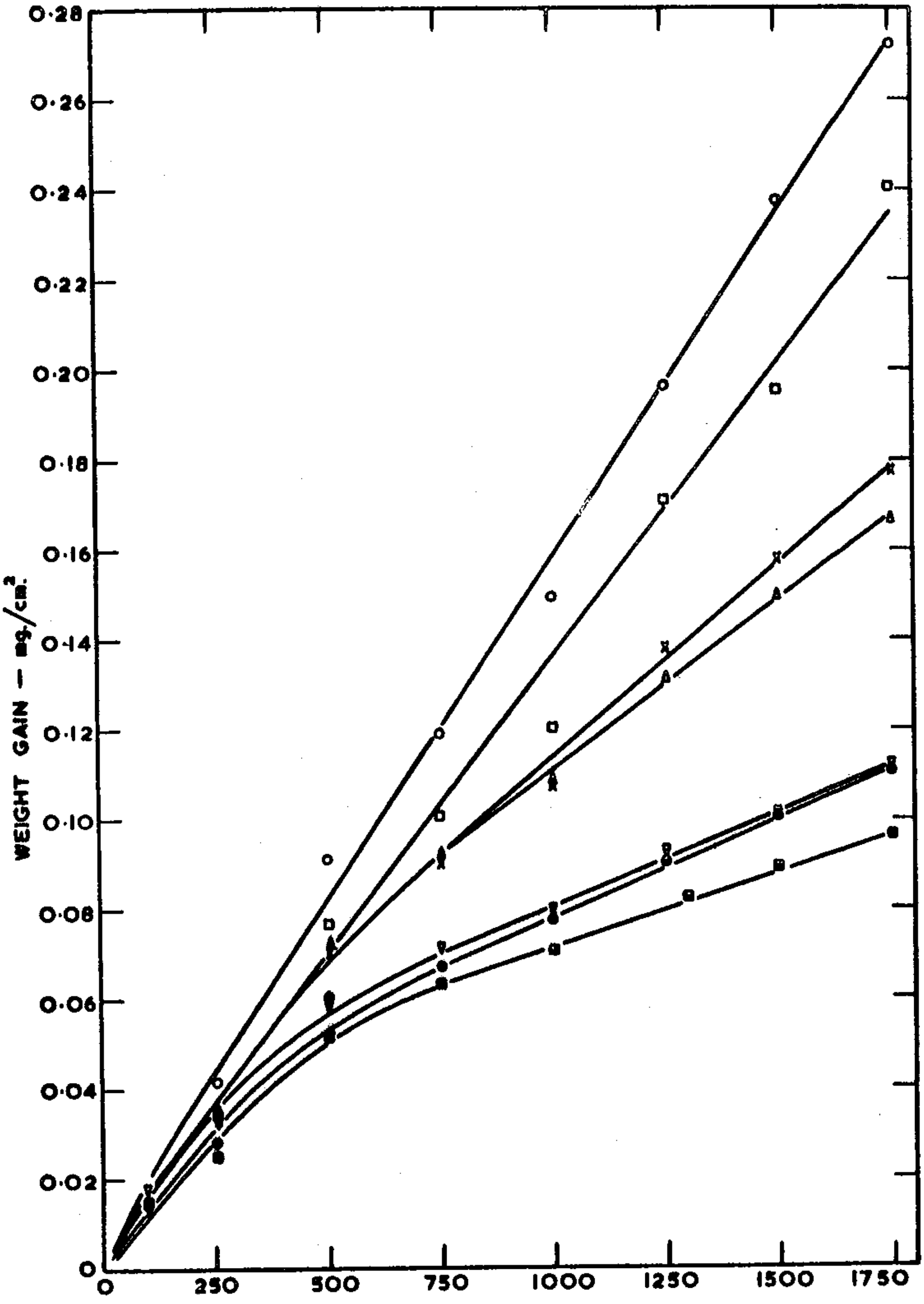


FIG 13 WEIGHT GAIN — TIME CURVES FOR INDIVIDUAL Be SPECIMENS IN CO_2 AT 675°C & 280 p.s.i.g.

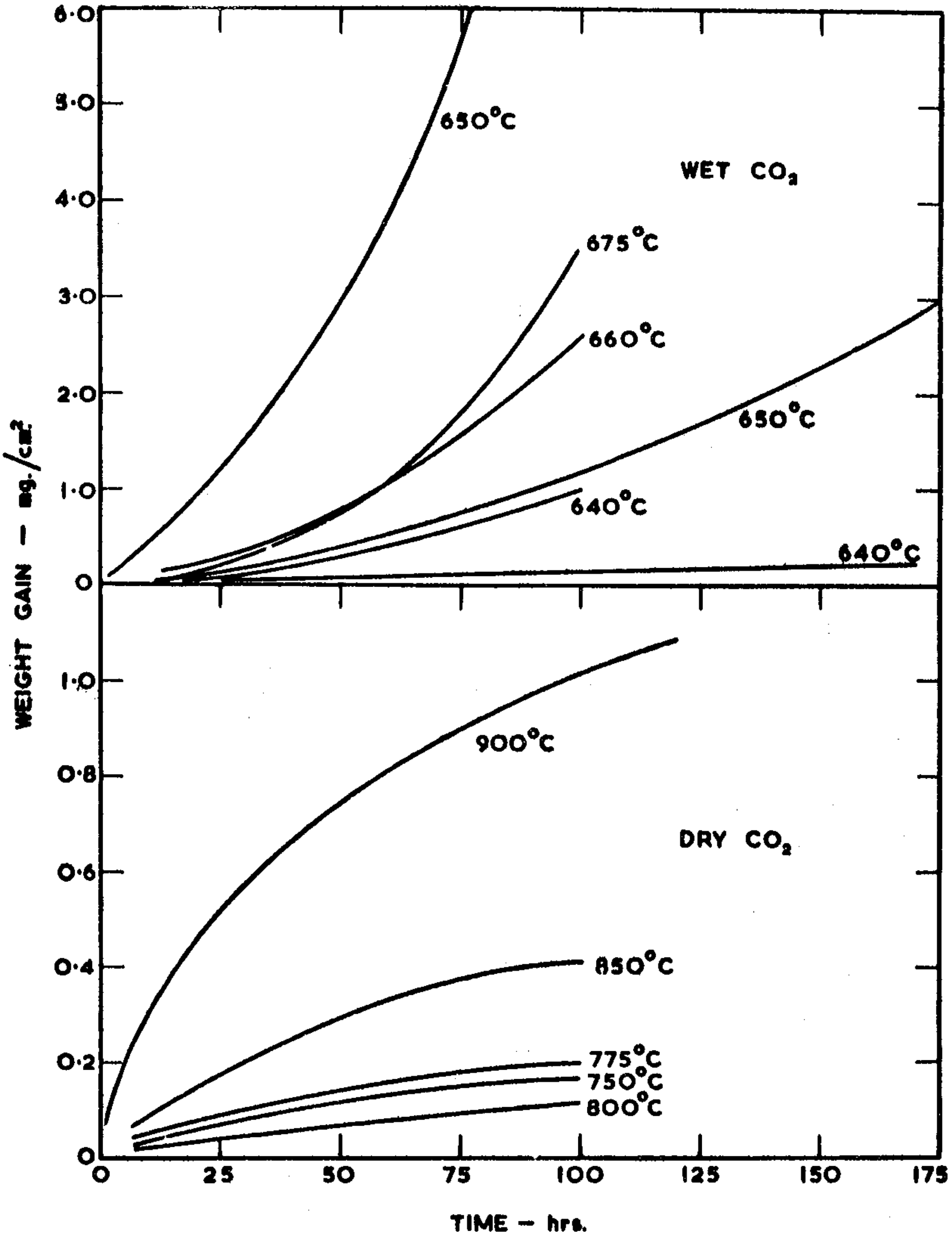


FIG. 14 WEIGHT GAIN DATA AT ATMOSPHERIC PRESSURE OF Be IN WET & DRY CO_2 ON STANTON THERMOBALANCES.

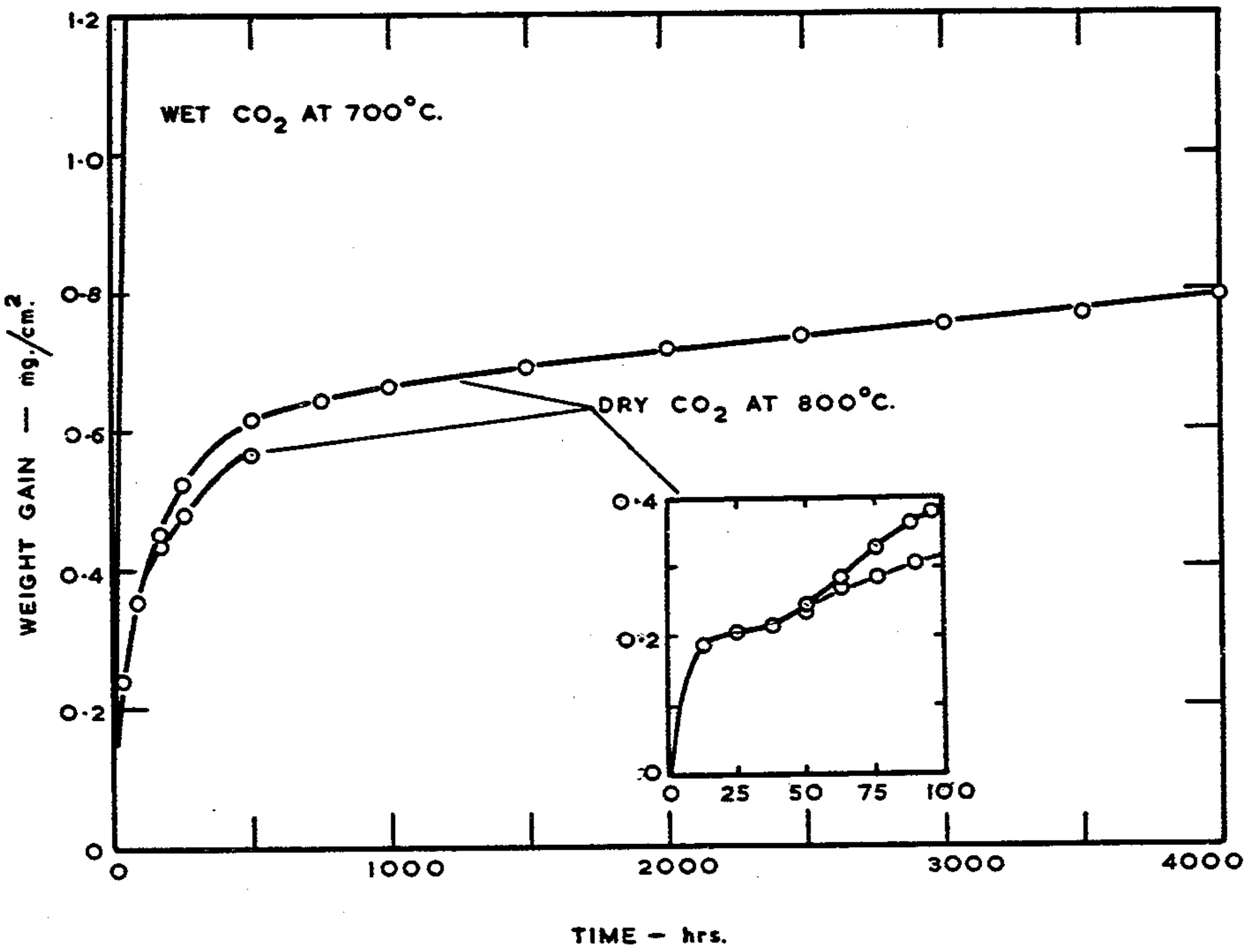


FIG. 15 WEIGHT GAIN CURVES OF Be IN WET & DRY CO_2 MEASURED ON QUARTZ FIBRE THERMOBALANCES.

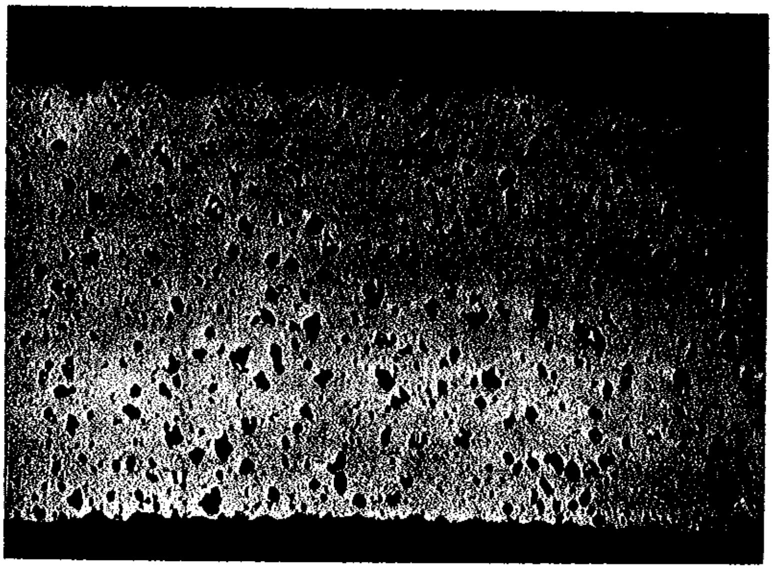


FIGURE 16 BERYLLIUM AFTER EXPOSURE TO DRY CARBON DIOXIDE AT 800 °C X 75

Weight Gain: 0.8 mg/cm^2 after 500 hours

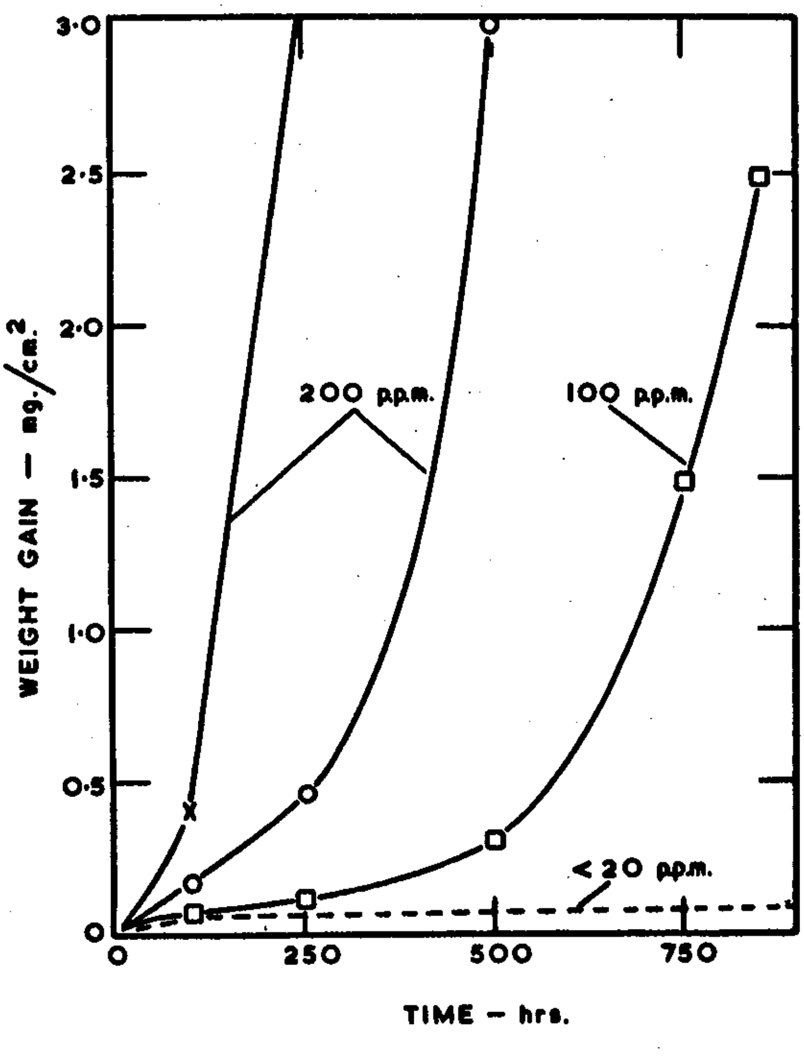


FIG. 17. WEIGHT GAIN—TIME CURVES SHOWING BREAKAWAY CORROSION OF Be IN MOIST CO_2 AT 625°C & 250 p.s.i.g.

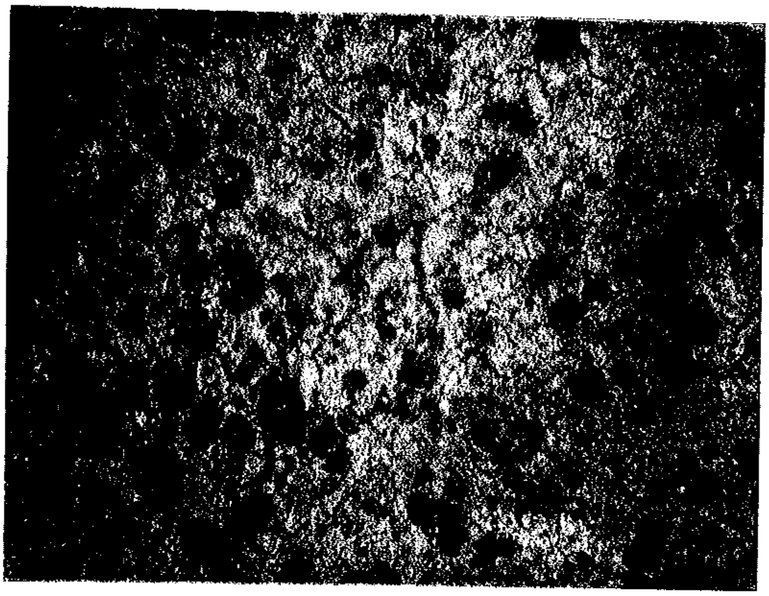
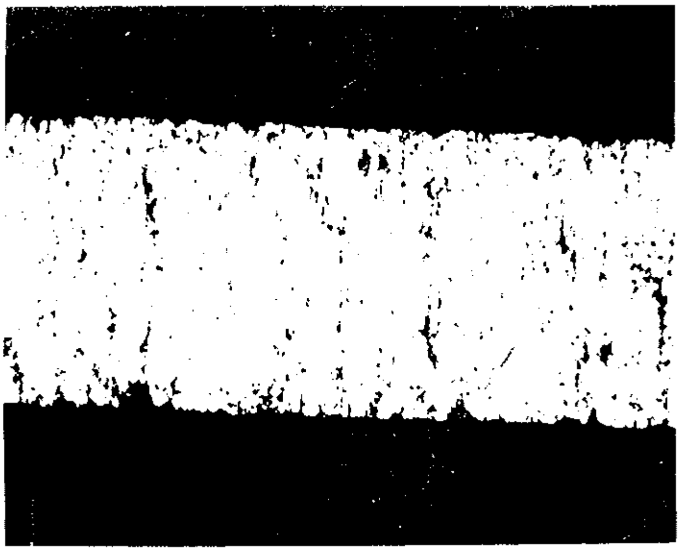


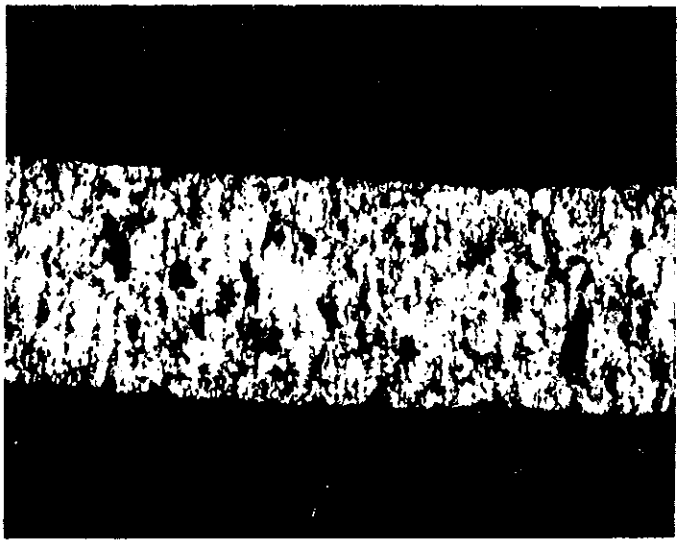
FIGURE 18 EXTERNAL SURFACE OF BERYLLIUM AFTER EXPOSURE TO WET CARBON DIOXIDE AT 700 °C X 100

Weight Gain: 10 mg/cm^2

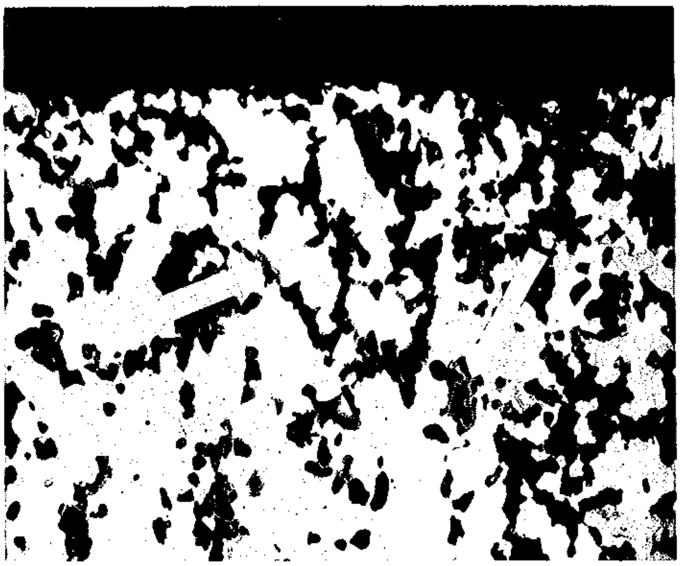


(a) Weight Gain: 0.8 mg/cm^2 X 75

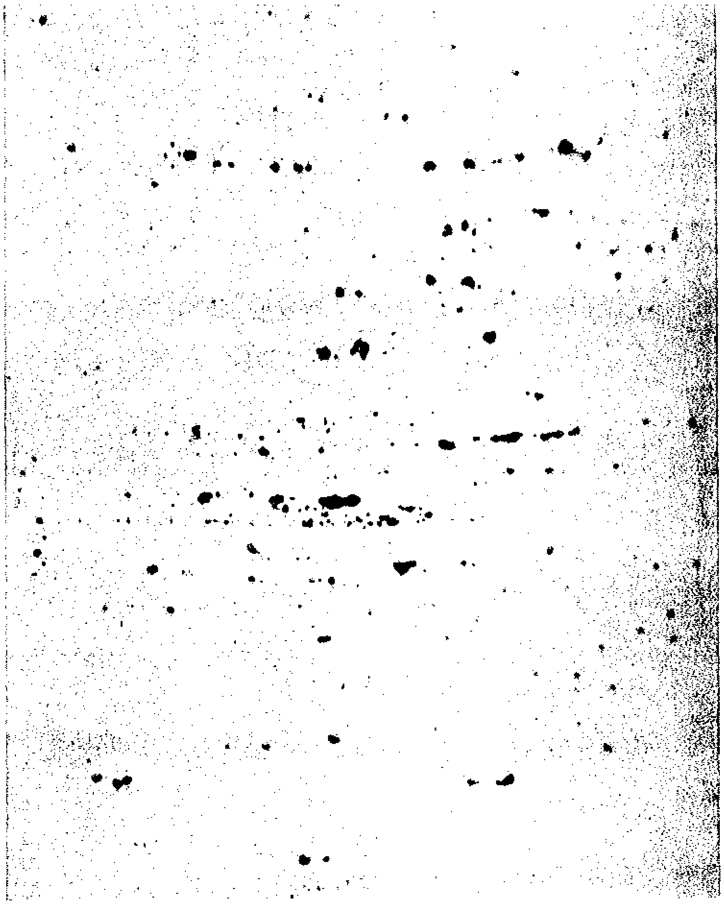
(b) Weight Gain: 3.2 mg/cm^2 X 75



(c) Weight Gain: 5.8 mg/cm^2 X 75



(d) Weight Gain: 5.8 mg/cm^2 X 250



(e) Weight Gain: 8.0 mg/cm^2 X 75

FIGURE 19 BERYLLIUM AFTER EXPOSURE TO WET CARBON DIOXIDE AT 700°C AND 1 ATMOSPHERE

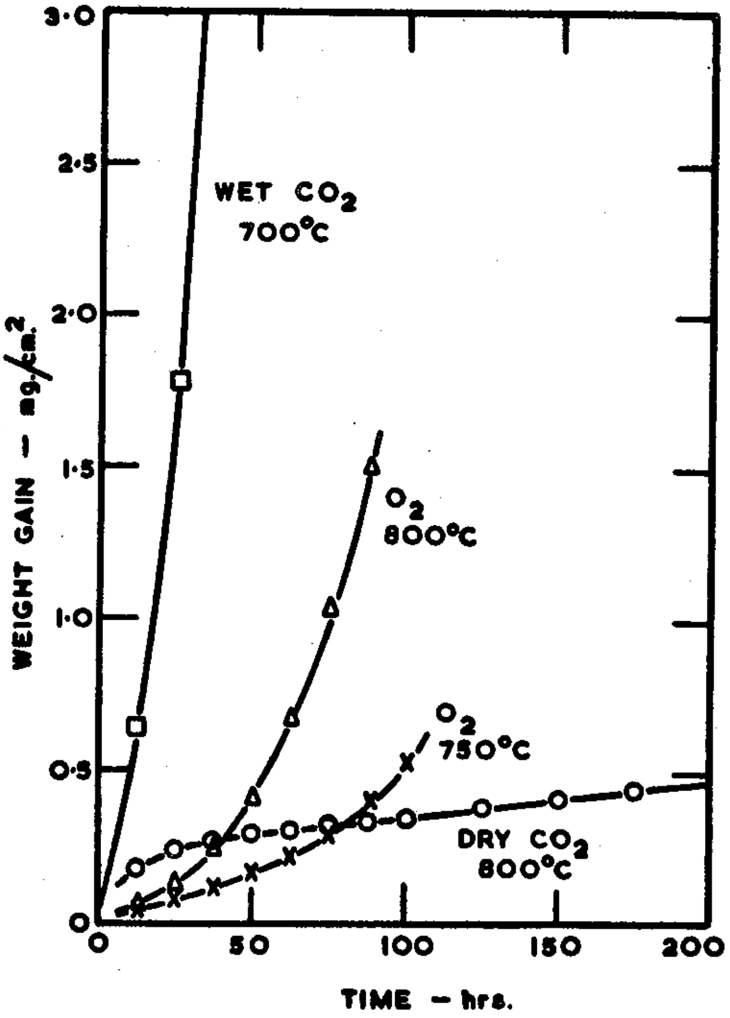


FIG. 20. WEIGHT GAIN CURVES OF Be IN WET & DRY CO_2 & DRY O_2 MEASURED ON QUARTZ FIBRE THERMOBALANCES.

FIGURE 21 EXTERNAL SURFACE OF BERYLLIUM AFTER EXPOSURE TO DRY OXYGEN AT 750°C X 100

Weight Gain: 1.65 mg/cm^2

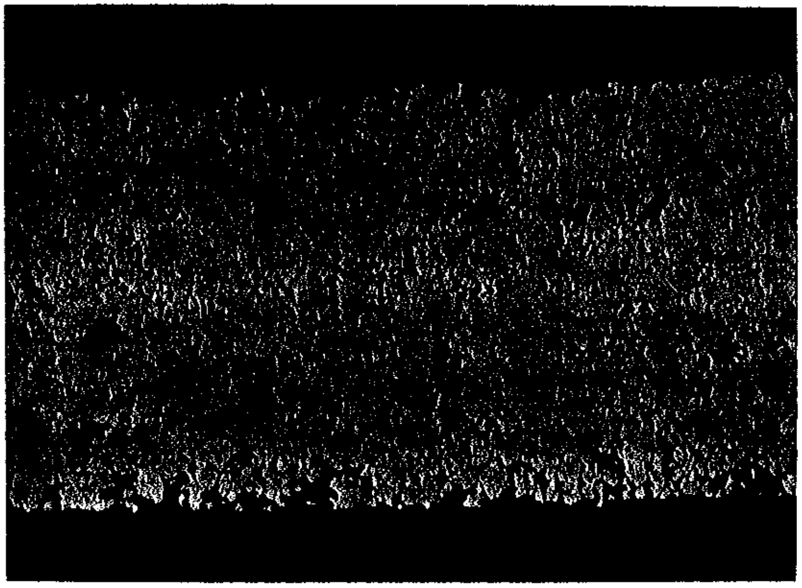
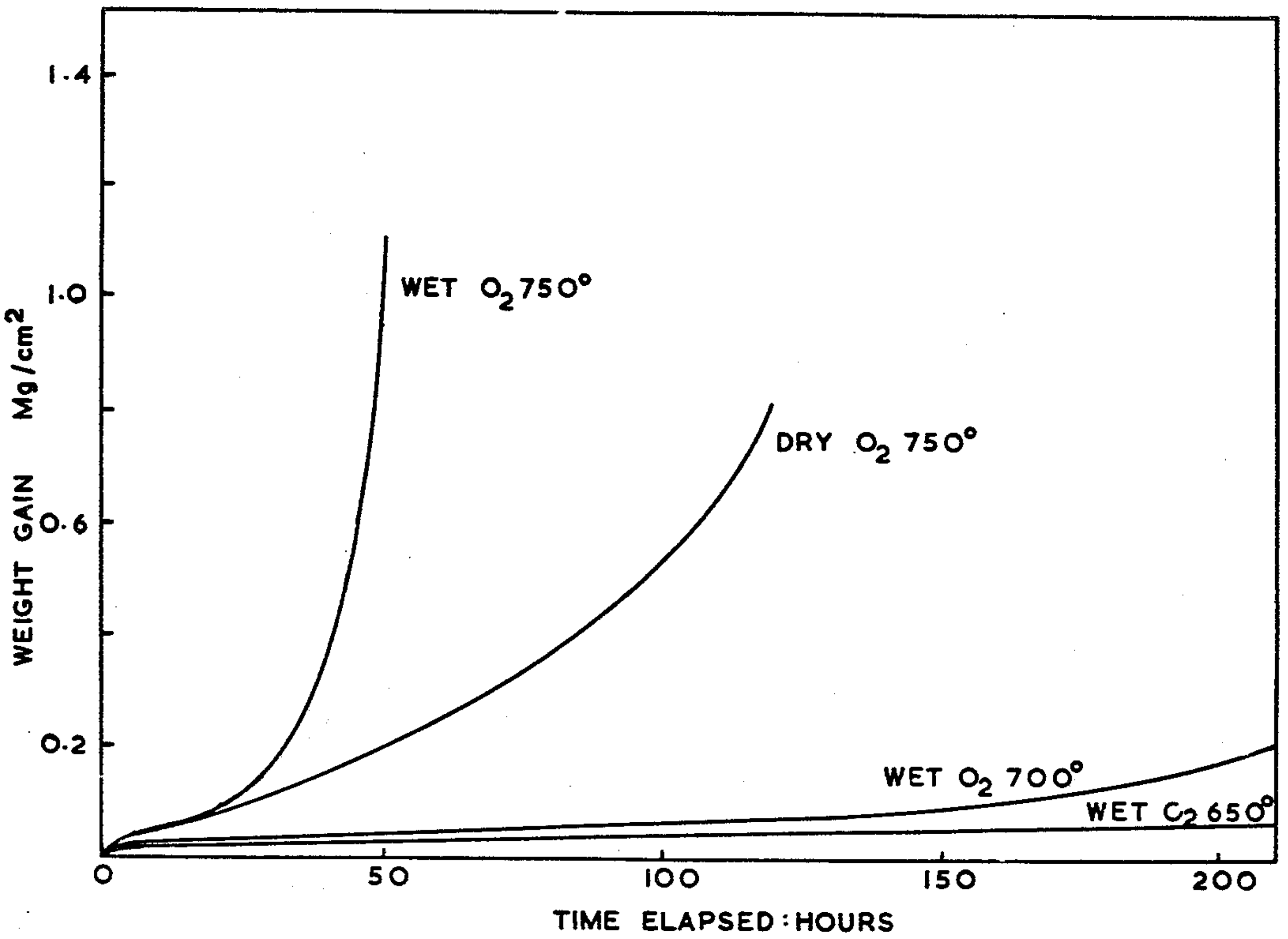


FIGURE 22 BERYLLIUM AFTER EXPOSURE TO DRY OXYGEN AT 750° C X 75

Weight Gain: 1.65 mg/cm^2 after 150 hours



WEIGHT GAINS OF BERYLLIUM IN WET AND DRY OXYGEN

FIGURE 23