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LOW PRESSURE OXIDATION OF COLUMBIUM-1 ZIRCONIUM

PRATT & WHITNEY AIRCRAFT
DIVISION OF UNITED AIRCRAFT CORPORATION
CANEL
MIDDLETOWN • CONNECTICUT

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ABSTRACT

The reactions of Cb-1 Zr alloy with oxygen were investigated at various temperatures and pressures. Continuous weight gain measurements were made using a vacuum thermobalance capable of detecting a 0.15 ± 0.05 mg weight change at temperatures up to 3500F from atmospheric pressure to 10^{-6}mm Hg. This data is presented for oxidation at 1000F, 1400F and 1600F from 1 x 10^{-3} to 1 x 10^{-5} mm Hg for 10-hour test periods. Corresponding quantitative internal oxidation measurements were performed to correlate hardness, penetration depth and oxygen content. The following reactions occurred sequentially: adsorption and solution of oxygen creating a dispersed ZrO_2 subscale by internal oxidation, formation of orientation dependent CbO, oxidation of CbO to CbO_2 and subsequent establishment of a continuous CbO_2 layer. This CbO_2 layer caused protective oxidation and directly affected the total weight gain and degree of oxygen penetration. CbO indirectly influenced protective oxidation behavior, since the quality of the CbO_2 scale apparently was related to the amount of CbO initiating CbO_2. Oxidation parameters are indicated for protective and nonprotective scale formation, and corresponding internal oxidation. Within the pressure ranges investigated, some of the most severe contamination occurred at the lowest pressures when CbO_2 scale was not produced. The structural changes, subscale and scale formation caused by oxidizing Cb-1 Zr alloy are illustrated schematically.

LOW PRESSURE OXIDATION OF COLUMBIUM-1 ZIRCONIUM

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April 20, 1964
DATE

INTRODUCTION

Previous investigations performed in the Materials Laboratory at CANEL concerned the oxidation of Cb-1 Zr alloy in air at various temperatures and the development of oxidation resistant columbium base alloys (1 and 2). Recent developments have established a need for data on the effects of low pressure environments on various refractory metals and alloys. The reactions with oxygen of one such alloy, Cb-1 Zr alloy, were investigated at various pressures and temperatures. Data will be presented for oxidation at 1000F, 1400F, and 1600F in the pressure range 1×10^{-3} to 1×10^{-5} Torr for 10-hour test periods. Continuous weight gain measurements were made using a vacuum thermobalance capable of electronically plotting weight changes as small as 0.15 ± 0.05 mg as a function of time. Apparatus was developed to accurately control oxygen pressure of the specimen at temperatures up to 3500F. As an example, a pressure of 5×10^{-5} torr $\pm 0.2 \times 10^{-5}$ torr could be easily maintained for entire test periods. A complete description of the experimental equipment and techniques is presented in a paper submitted for publication to the Journal of Scientific Instruments (3). It is important to note that bulk specimens (0.375 inch diameter right cylinders 0.500 inch high) were used in this study. Previous investigations such as that of Inouye (4) on low pressure oxidation of pure columbium employed the use of thin (10 mils) sheet specimens. A preliminary investigation by the authors of pure columbium at low pressure (5) showed oxygen penetration at low pressures is extensive. Since subsequent reactions depend on the formation of an oxygen concentration gradient in the specimen, true kinetics can not be determined unless a C_0 (original concentration of oxygen in the specimen) is maintained. This is impossible in thin sheet specimens. Quantitative internal oxidation analysis was performed by hardness measurements correlated with oxygen content and penetration determined by micro-machining techniques and vacuum fusion analysis.

EXPERIMENTAL RESULTS AND DISCUSSION

The following reactions occurred sequentially as shown schematically in Fig. 1: adsorption and solution of oxygen in the matrix accompanied by corresponding precipitation of ZrO_2 particles, formation of orientation-dependent CbO, oxidation of CbO to CbO_2, and establishment of a continuous CbO_2 layer. These reactions could be studied independently by varying the oxygen pressure as shown in Fig. 2 for tests at 1600F.

The initial portion of the continuous weight gain curves from 1×10^{-3} torr to 5×10^{-5} torr correspond to solution of oxygen, precipitation of dispersed ZrO_2 particles, and subsequent CbO formation just below the surface. At 3×10^{-5} and 1×10^{-5} torr only solution of oxygen occurred, no CbO was formed. No rate change was found when CbO did form, its formation being a function of the oxygen concentration in solution and orientation dependence. CbO formation at 5×10^{-5} torr is shown in Fig. 3. CbO can be seen as nodules and grain boundary phase. The fact that some matrix grains are completely surrounded by CbO suggests the orientation of these grains is not favorable for conversion to CbO. At 8×10^{-5} torr and 1×10^{-4} torr, CbO_2 begins to form from oxidation of CbO at the surface. The formation of CbO leads to complex parabolic rates; however, at these pressures a continuous scale is not produced. Rates are therefore a mixture of linear where CbO_2 has not formed on the matrix and parabolic where CbO_2 formed on CbO; resulting weight gain is greatest. The formation of CbO_2 from the oxidation of CbO only, is shown in Fig. 4 for a test run at 1×10^{-4} torr. At 5×10^{-4} torr and 1×10^{-3} torr the formation of CbO_2 occurs rapidly producing a CbO_2 continuous scale. This results in characteristic protective oxidation and complex parabolic rates. Total weight gain is less than that found at 5×10^{-5} torr. A typical continuous CbO_2 scale produced a 1×10^{-3} torr is shown in Fig. 5.

A similar reaction sequence is found at 1400F as a function of pressure, Fig. 6. Total weight gains are less than at 1600F as would be anticipated. Again total weight at 5×10^{-4} torr is less than some lower pressures as a result of CbO_2 scale formation. The higher weight gain at 1×10^{-3} torr found at 1400F can be explained by considering the character of the CbO_2 scale formed. Unlike CbO_2 scales formed at the same pressure at 1600F, this scale was of a powdery nature and as the weight gain versus time curve shows, not as protective. The character of the CbO formation at 1400F was also different. Very little CbO was present adjacent to the surface as nodules, columbium grains converted to CbO; instead, CbO formation in specific crystallographic directions in columbium grains was evident as shown in Fig. 7. It is interesting to note that as a result of change in orientation of preferred growth planes from one grain to the next, CbO well below the surface in one grain can initiate growth in an adjacent grain in a direction opposite to the diffusion of oxygen. It is believed that at 1400F the majority of CbO_2 forms from the oxygen saturated matrix rather than from the oxidation of CbO, thus producing the observed difference in scale character.

At 1000F, no scales were produced, all weight gain resulting from oxygen solution,as a result, weight gain varied directly with pressure, Fig. 8.

The effect of a CbO_2 continuous scale on the total weight gain in itself is not sufficient to describe the reaction completely. Since at low pressures a great deal of weight gain can be attributed to oxygen in solution, the effect of a CbO_2 scale on total oxygen penetration must be considered. An example of this effect is depicted in Fig. 9. The amount of oxygen in solution (represented by the area under the concentration curve) and the degree of penetration at 5×10^{-5} torr, where no CbO_2 scale is formed, is greater than at 1×10^{-3} torr where the protective CbO_2 scale prevents excessive penetration. The oxygen in solution depicted here resulted mostly prior to CbO_2 continuous scale formation. Very little advance of the gradient was observed after a CbO_2 scale had formed.

SUMMARY

It has been shown that arbitrarily lowering the pressure at a specific temperature to prevent oxygen contamination of Cb-1 Zr alloy is not the complete answer. A knowledge of reaction characteristics in respect to rate of weight gain, oxygen penetration, and oxides formed as a function of pressure, temperature, and time must be acquired before valid engineering recommendations can be made.

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SCHEMATIC REPRESENTATION OF LOW PRESSURE OXIDATION OF Cb-1 Zr

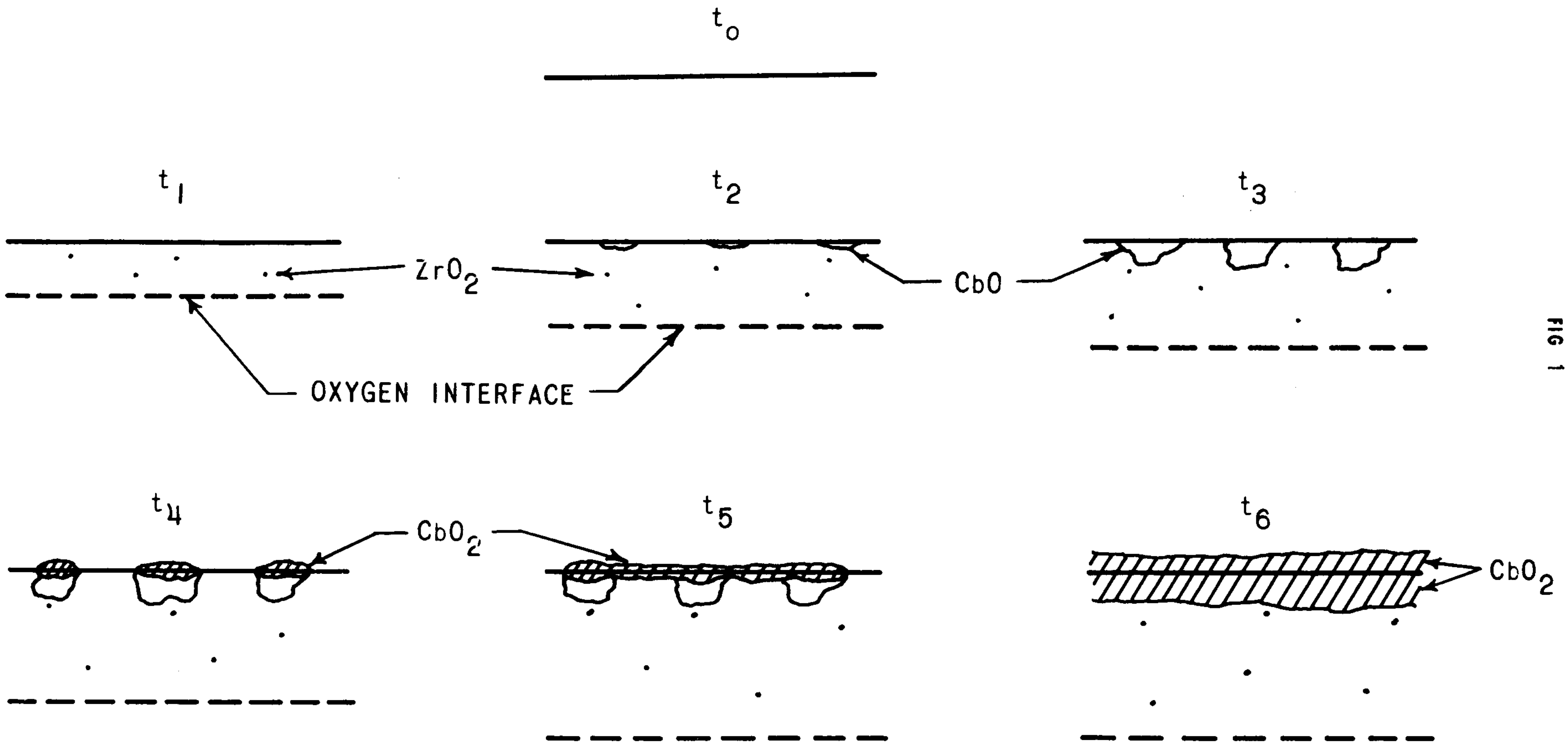


FIG 1

CONTINUOUS WEIGHT GAIN AT 1600F

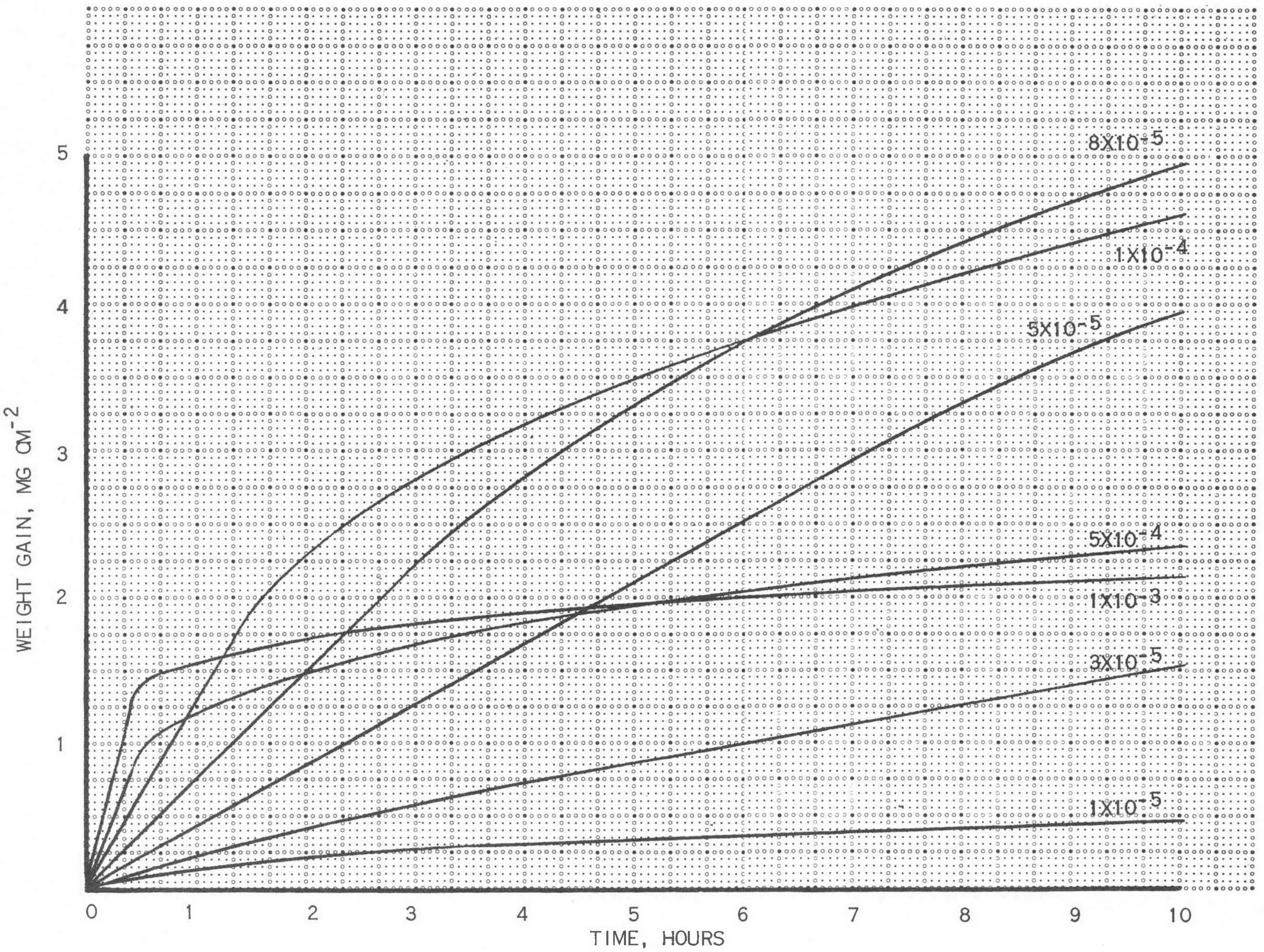
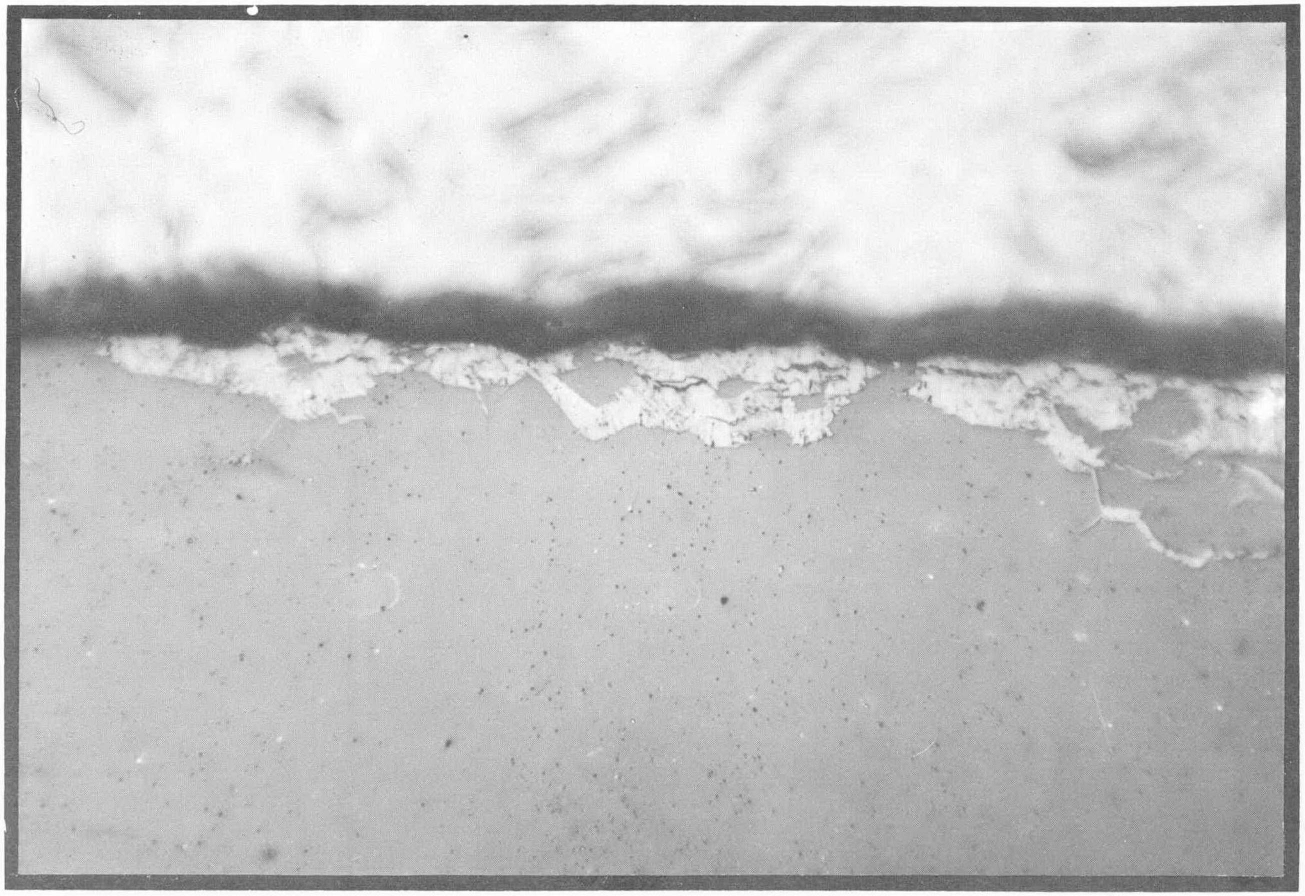


FIG 2

CbO FORMATION AT 5×10^{-5} TORR



MARGOLIN-ENCE STAIN ETCH

MAGNIFIED: 500X

FIG 3

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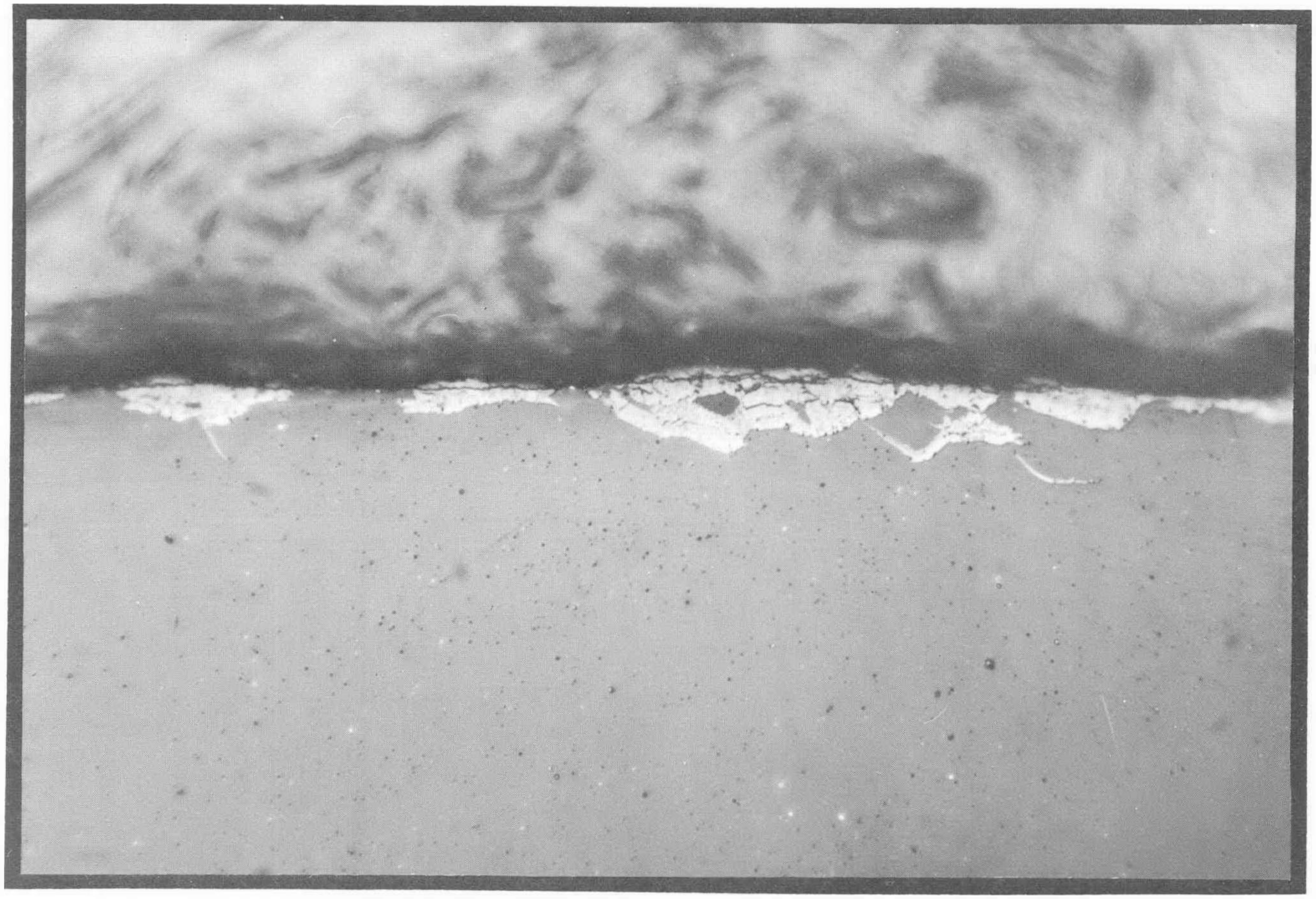
FORMATION OF CbO_2 FROM THE OXIDATION OF CbO, 1 X 10^{-4} TORR



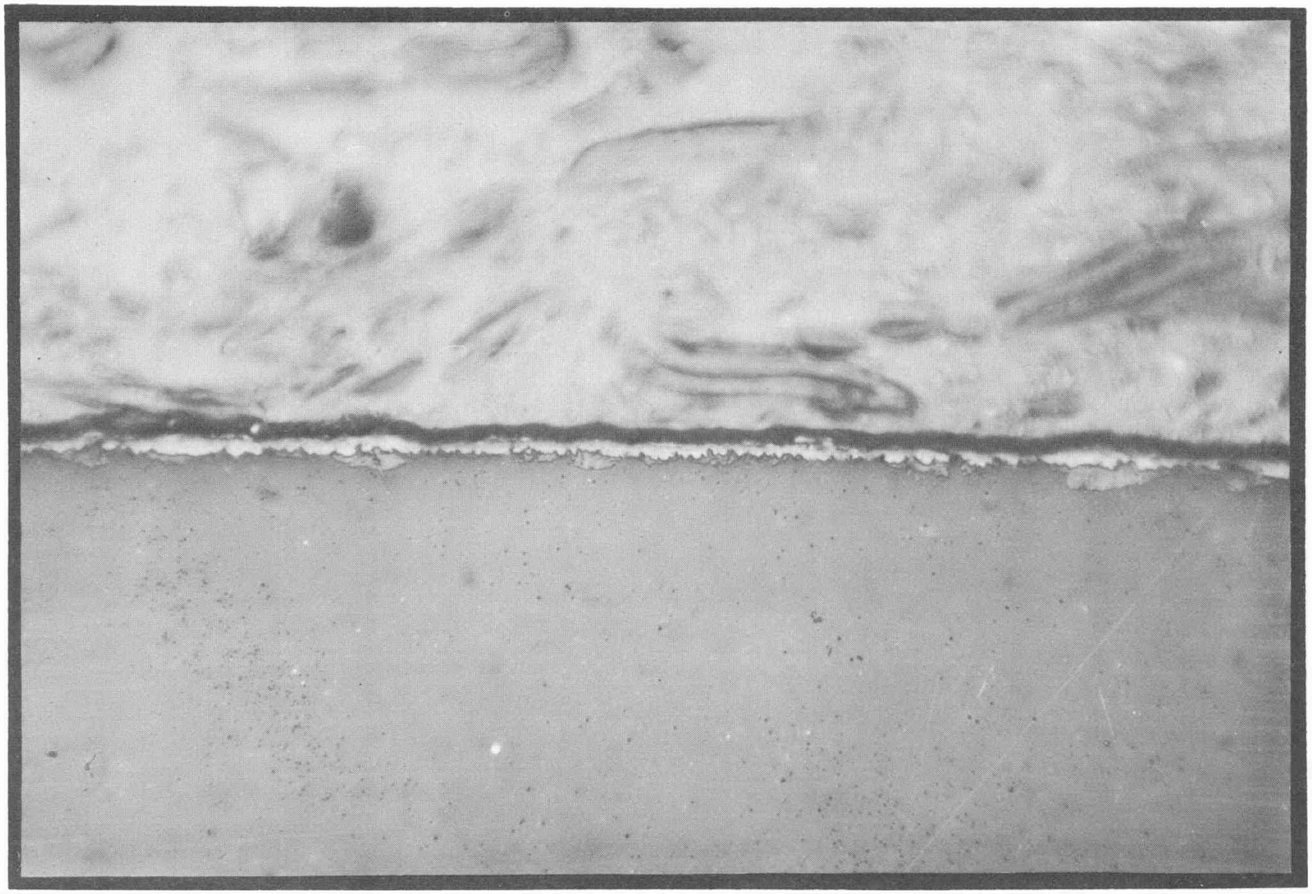
MARGOLIN-ENCE STAIN ETCH

MAGNIFIED: 500X

FIG 4

2826-3

TYPICAL CONTINUOUS CbO_2 SCALE PRODUCED AT 1 X 10^{-3} TORR



MARGOLIN-ENCE STAIN ETCH

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FIG 5

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CONTINUOUS WEIGHT GAIN AT 1400F

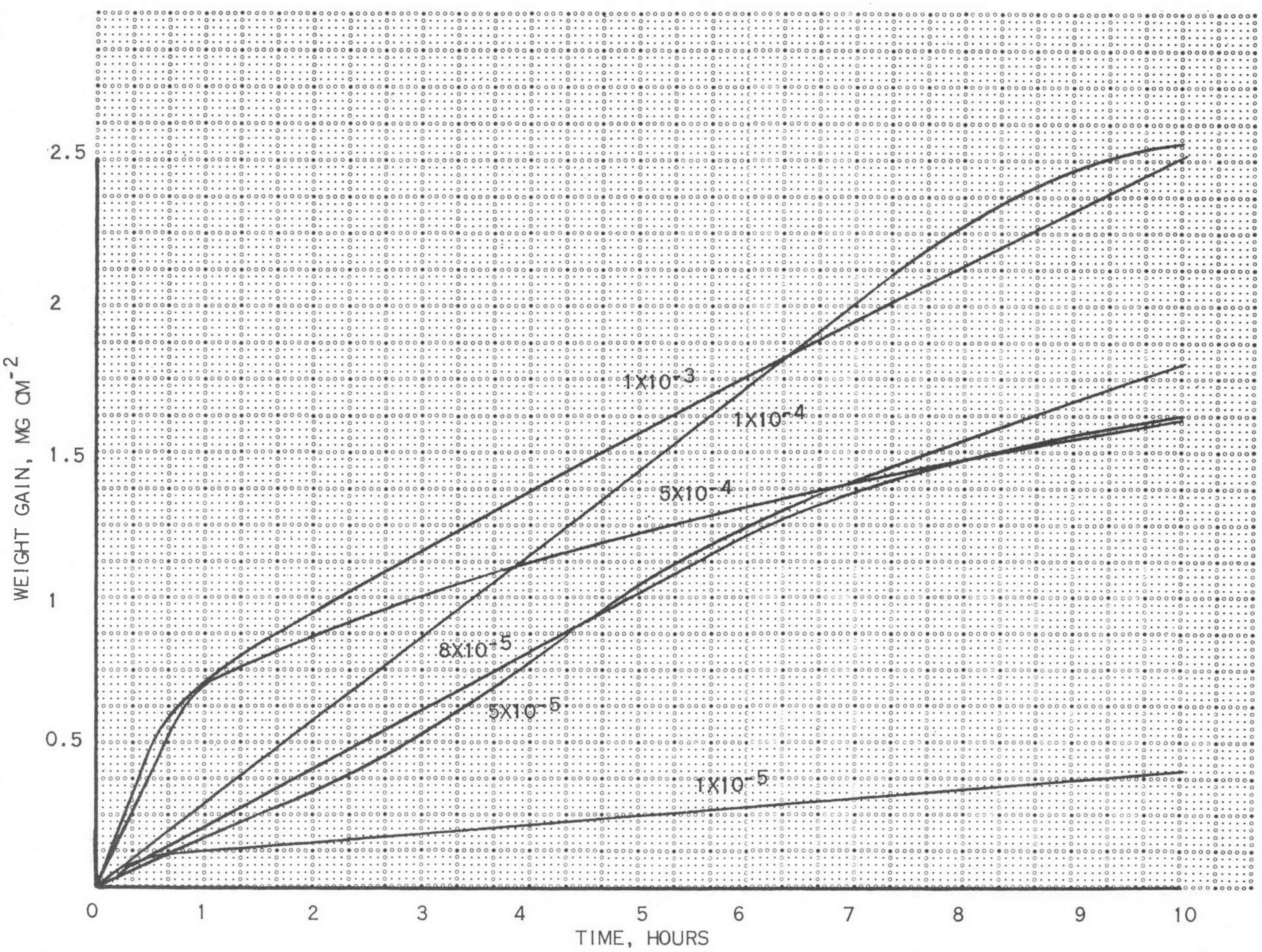
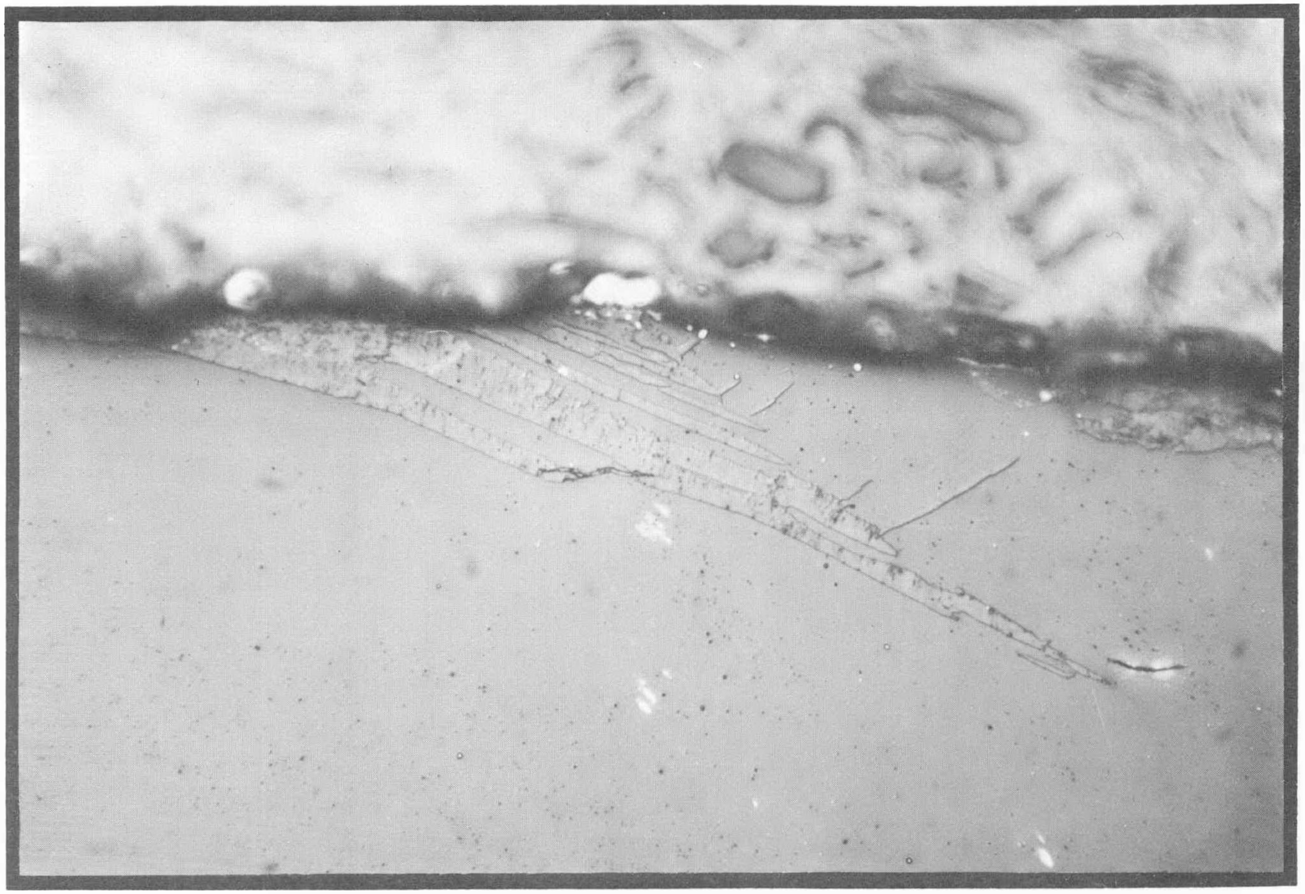


FIG 6

FIG 7

CRYSTALLOGRAPHIC ORIENTED CbO PRODUCED AT 1400F AND 1 X 10^{-4} TORR



MARGOLIN-ENCE STAIN ETCH

MAGNIFIED: 500X

2826-6

CONTINUOUS WEIGHT GAIN AT 1000F

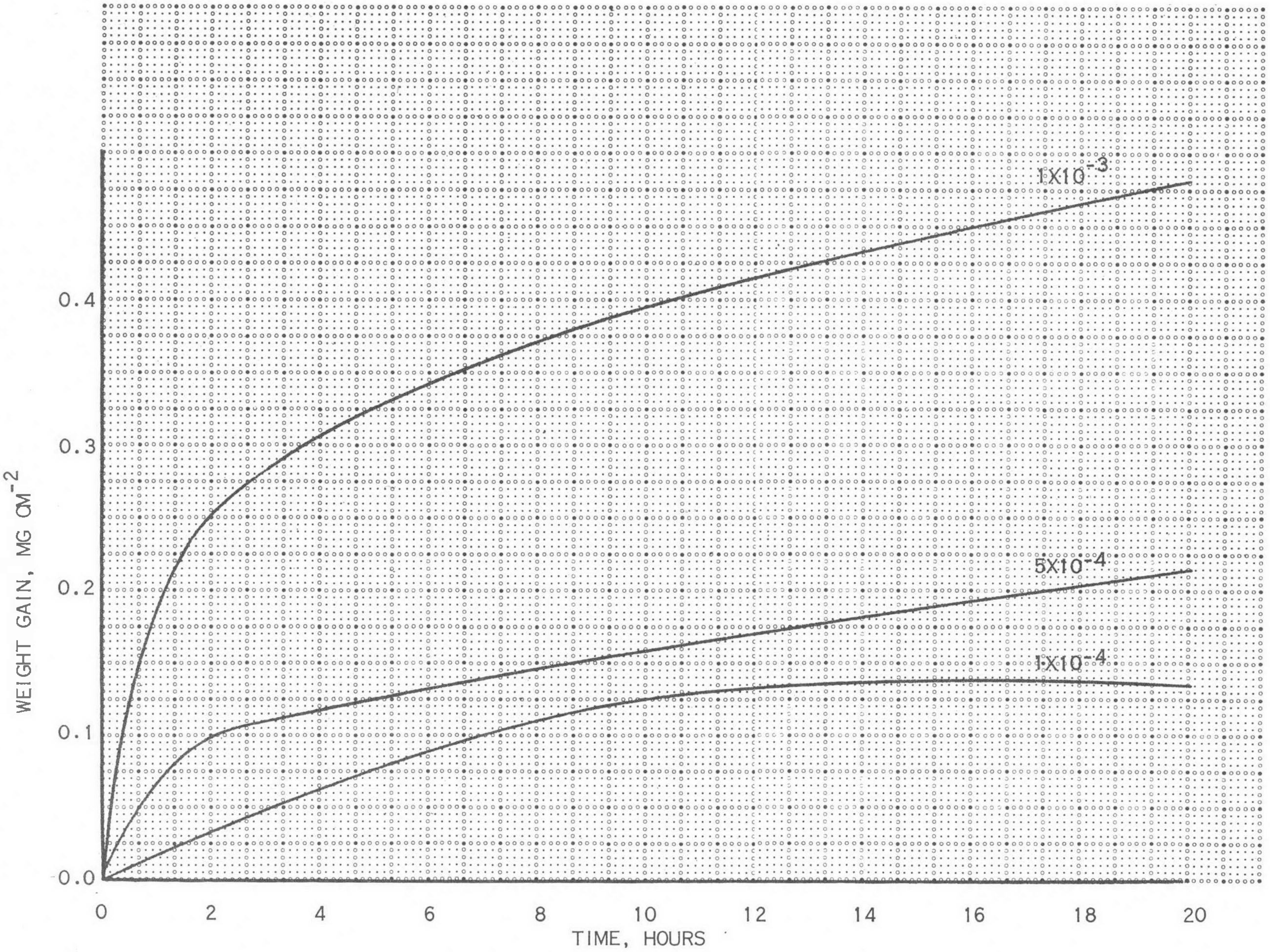


FIG 8

OXYGEN PENETRATION OF Cb-1 Zr AT 1600F

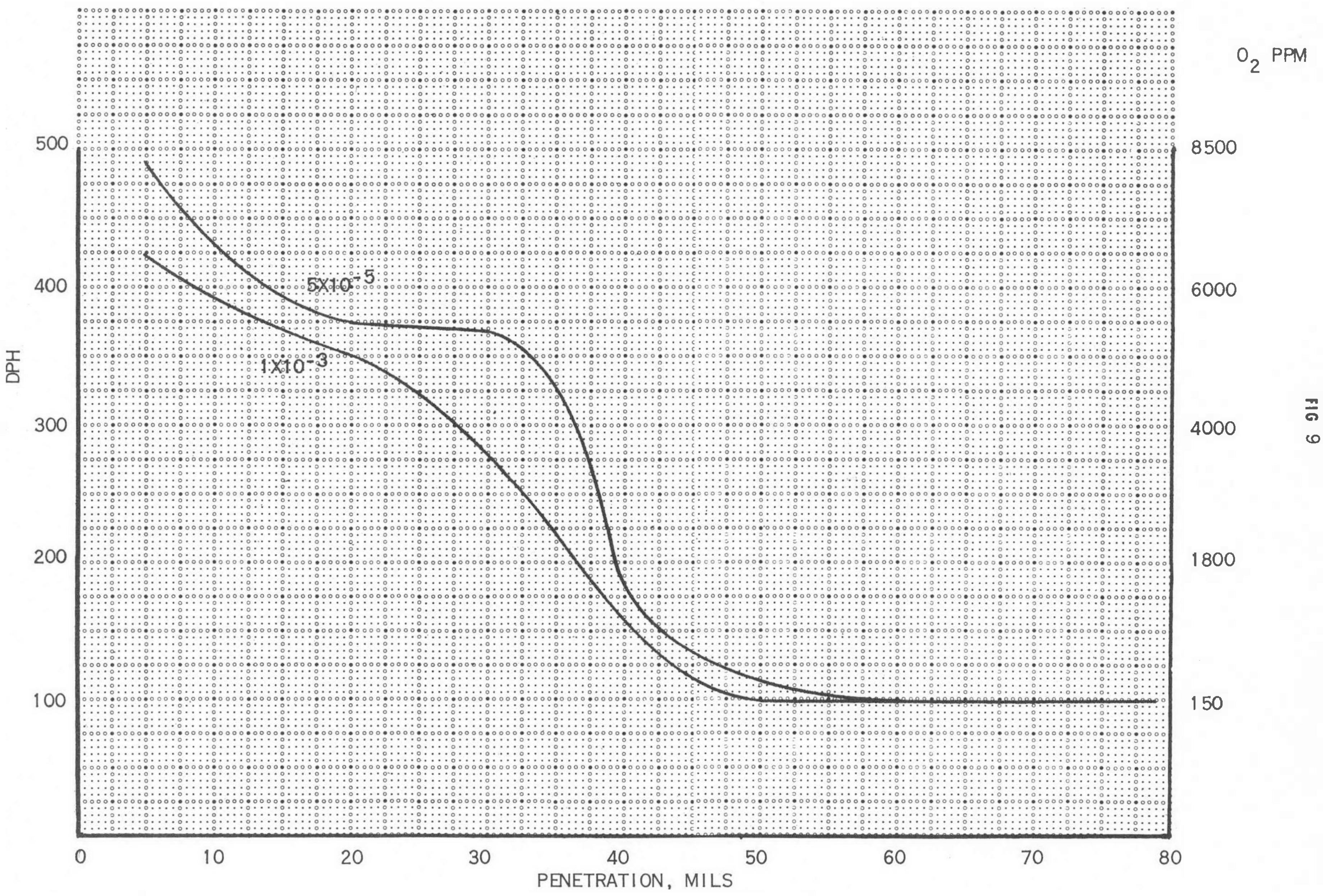


FIG 9