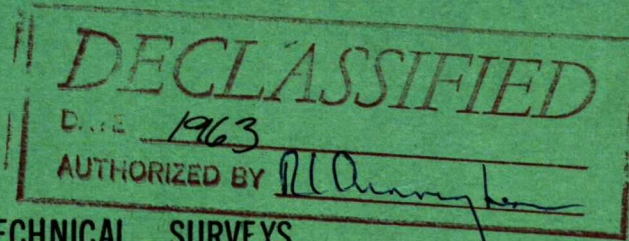


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THE MECHANISM OF OXIDATION IN TITANIUM

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SUMMARY

The mechanism of the oxidation of pure titanium metal had been investigated at 830°C and 940°C. A tracer of tantalum -182 was used to mark the original metal surface and it was confirmed that oxidation takes place by inward diffusion of oxygen ions to the metal-oxide interface. The reaction rate follows a parabolic law, but is greatly affected by the porosity of the oxide layer formed. X-ray diffraction patterns indicate that the composition of the oxide layer varies with temperature and rate of formation.

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INTRODUCTION

Great interest has arisen in the properties of titanium in recent years because of its strength, lightness, and resistance to corrosion. However, one of the limiting factors in the use of titanium is its ready oxidation at high temperatures.

The oxidation of metals is essentially a diffusion process which proceeds by one of four mechanisms: the metal cations may diffuse through the oxide layer to the oxide-gas interface, or the oxygen anions may diffuse through the oxide layer to the metal-oxide interface. In the first instance the diffusion would proceed by means of cation vacancies in the oxide; i.e., the motion of metals cations from, say, right to left, might be looked upon as the motion of vacancies from left to right. Similarly, the diffusion of oxygen ions would occur by means of anion vacancies. Likewise, an interstitial diffusion mechanism is possible with either cations or anions as the diffusing species.

The mechanism obtaining for the oxidation process may be ascertained by placing a tracer on the surface of the metal prior to oxidation. The tracer will remain at the metal-oxide interface if the oxidation proceeds by the outward diffusion of metal ions, and will remain at the oxide-gas interface if oxygen ions are the diffusing components in the oxide.

This method has been applied to titanium by Davies and Birchenall⁽²⁾, who used silver as a tracer, but their experiment was not very

conclusive because their tracer could not be found after the oxidation had run its course. However, these authors postulated that the silver had remained at the oxide-gas interface throughout the oxidation but had evaporated off in the four days required to form thick scales at 900°C; they thus put forward the mechanism of anion diffusion, and inasmuch as the titanium dioxide formed is oxygen-deficient, the range in composition corresponding to the rutile lattice being $\text{TiO}_{1.9}$ - $\text{TiO}_{2.0}$ ⁽³⁾, this is the reasonable mechanism to suggest and indeed has been confirmed by the present investigation.

The main subject of the present study was the mechanism of the reaction; rate studies have been carried out previously, (2, 4). Carpenter and Reavell (1), following the course of the reaction by essentially the same technique as that used in this research, reported that the rate of the reaction, as determined by a plot of oxygen pressure against time, is not very sensitive to oxygen pressure. They had worked at oxygen pressures of one fiftieth of an atmosphere and at temperatures between 700°C and 1000°C. Kinetic studies are complicated by a phase transition which occurs at 880°C in the pure metal, and by the great solubility of oxygen in titanium, forming what does not seem to be a chemical compound in the usual sense, and what has indeed been referred to by some investigators as a titanium-oxygen alloy (6). Davies and Birchenall, for example, found that 36% of the oxygen taken up in an oxidation proceeding for one hundred minutes at 900°C had gone into solution in the metal, even assuming a stoichiometric composition of TiO_2 for the oxide formed.

EXPERIMENTAL DETAILS

The titanium used in the present investigation was cold-rolled iodide titanium (H 0.019% wt: O 0.018% wt, as determined by vacuum fusion analysis). After being rolled to a thickness of 40 mils, the metal was vacuum annealed for one hour at 1000°C. After annealing the metal had a Brinell hardness of 99, roughly the same as that of the very pure titanium prepared by Jaffee (5). Dissolved gases such as nitrogen or oxygen, and cold rolling as well, increase the hardness of the metal.

Tantalum -182 was employed as the tracer because of its very high boiling point and hence very low vapour pressure under the conditions of the experiment. Since electrodepositing tantalum onto titanium would have been very difficult if not impossible, without the use of other metals to form an intermediate layer, the tracer was applied by evaporating a few drops of a tantalum nitrate solution (20 μ c/ml) on a titanium strip. The sputtering technique could not be used because of the very high boiling point of tantalum (4100°C).

The titanium metal strips, with the evaporated tantalum nitrate on them, were heated in vacuo at 500°C for 24 hours to decompose the nitrate and procure a well-adhering thin deposit of tantalum oxide; after this treatment the activity of the tantalum deposit was not decreased appreciably by rubbing the surface of the titanium samples with emery paper.

The apparatus used is shown in Figure 1.

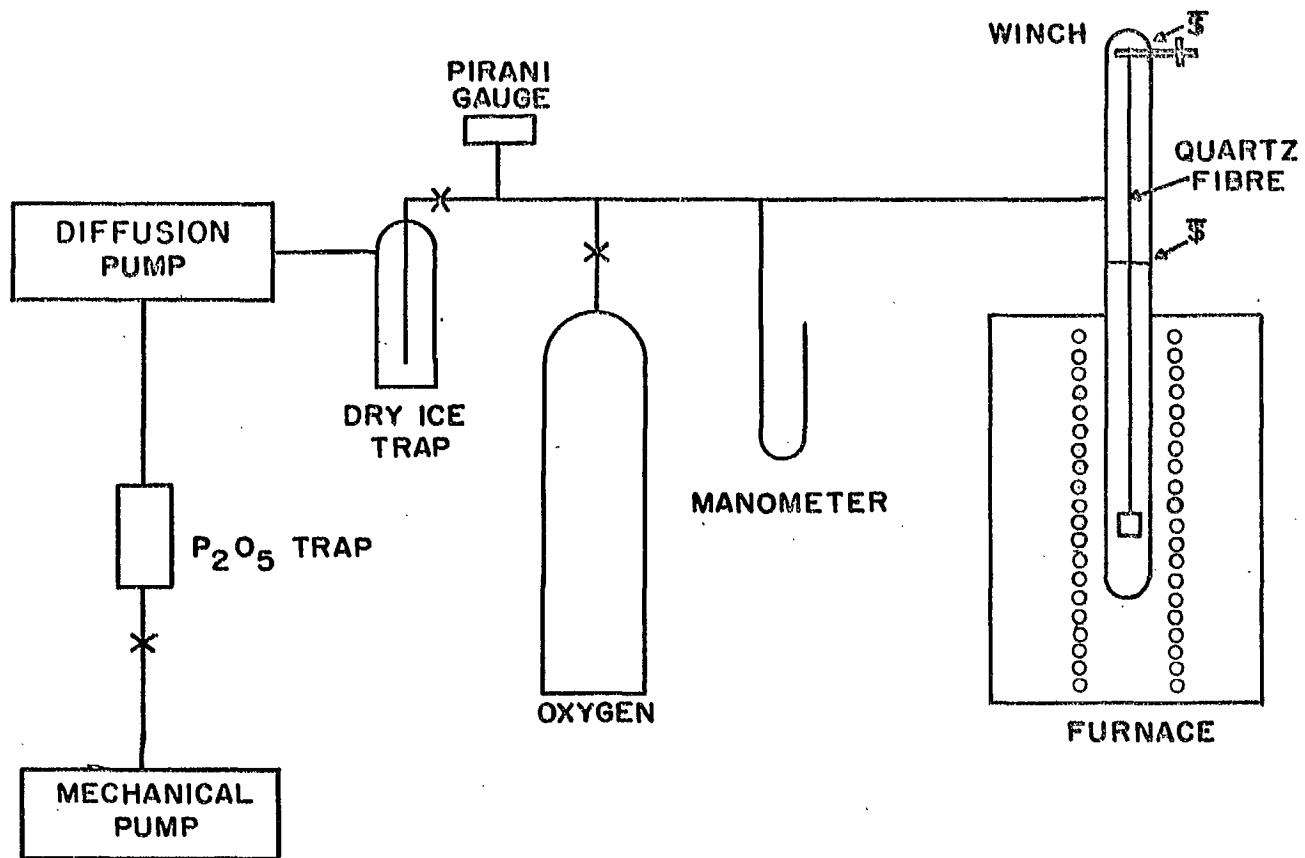


DIAGRAM OF APPARATUS
FIG. 1

The furnace was made of quartz and was 32.5 cm long and 3.75 cm diameter. The samples, 16 x 9 x 1 mm in size, were placed in the furnace tube, the system was evacuated, and the furnace brought to temperature. Oxygen was then introduced until the desired pressure was reached.

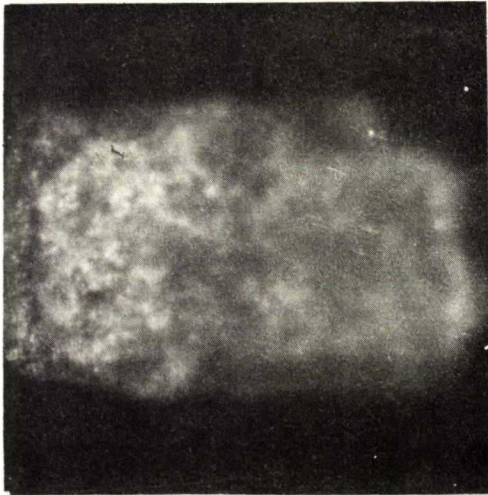
After oxidation, the oxide film was stripped from the metal and the activity present in the oxide and that remaining on the metal surface were determined. At both temperatures at which the reaction was studied (830° and 940°C), the activity remaining on the metal itself was negligible, and 85% of the original activity was on the surface layer. The actual figures are given in Table 1.

TABLE 1

Temp °C	Initial activity	Activity after oxidation (c/m)	
		metal	oxide
830		384	1920
830	7424	300	6400
940	12800	1000	11300
940	18200	750	15400

Figure 2 shows autoradiographs taken (a) of a metal sample prior to oxidation, and (b) of the stripped oxide layer after oxidation; they are seen to be identical.

The radioactivity of the samples was determined by placing them over the detector of a scintillation counter; the same geometry was maintained for each determination.



(a) Ti metal

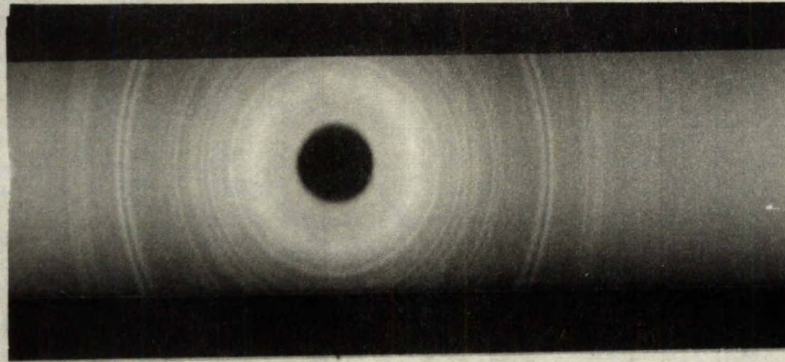
(b) oxide scale

Figure 2 - Autoradiographs (a) Ti metal (b) oxide scale

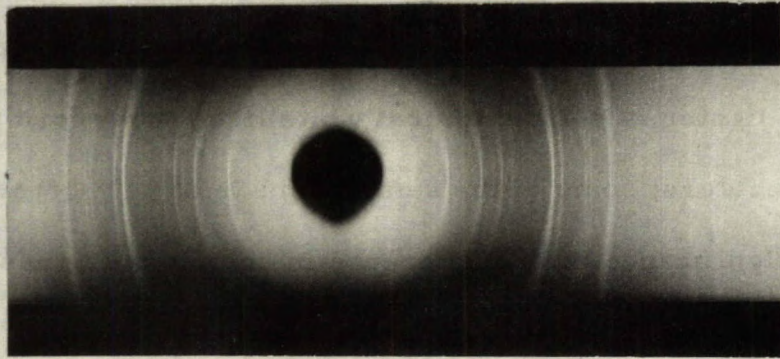
The oxide layers formed at the lower temperature, i.e., more slowly, were lighter in colour (almost white) than those formed at the higher temperature; some of the samples made at 940°C were deep blue. The significance of the difference in colour is discussed below.

COMPOSITION OF THE OXIDE LAYER

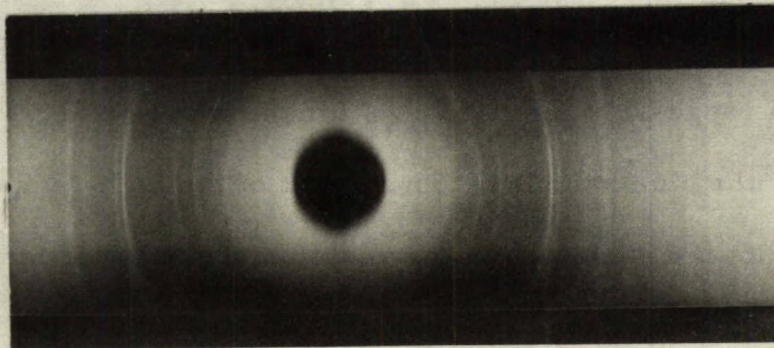
X-ray diffraction data from the powdered scales indicate both the white and blue scales to be rutile, with the white coloured one richer in oxygen, in accord with Ehrlich's data (3) on the influence of composition on colour. The patterns correspond to a stoichiometric composition range $\text{TiO}_{1.99}$ - $\text{TiO}_{1.98}$ for the white oxide, and $\text{TiO}_{1.95}$ - $\text{TiO}_{1.96}$ for the blue samples. The result of the high-temperature reaction is not the same as for the reaction at the lower temperature. The d and I values for the two types of oxide scales are given in Table 2. The actual spectra are shown in Figure 3.



(a) Black Powder Scraped from Scale



(b) White Scale, Oxidized at 830°C



(c) White Scale Oxidized at 940°C

Figure 3 - X-Ray Diffraction Spectra

Table 2

Debye Photograph of Patterns of Oxide Layers

Black Scale		White Scale		TiO ₂	
d	I	d	I	d	I
3.3	0.2				
3.25	0.22				
3.17	6	3.2	8	3.245	100
2.49	0.2				
2.46	6	2.48	7	2.489	41
		2.29	3	2.297	7
2.18	6	2.19	6	2.188	22
		2.03	3	2.054	9
1.83	0.2	1.87	0.5		
1.68	10	1.68	10	1.687	50
1.63	8	1.63	7	1.624	16
		1.58	0.5		
		1.53	0.2		
1.47	0.6	1.48	5	1.480	8
1.44	6	1.45	5	1.453	6
1.36	br 7	1.36	6	1.360	16
		1.34	5	1.347	7
1.30	0.2			1.305	1
1.23	0.2	1.25	1	1.243	3
				1.200	1
1.17	0.2	1.17	0.2	1.170	4
1.15	0.2	1.15	2	1.1485	4
				1.133	1
1.09	3	1.095	3	1.093	4
1.07	0.2	1.07	3	1.082	4
1.04	7			1.042	5
				1.036	4
		0.965	0.5	0.964	2
.905	1	0.91	1	0.907	3
		0.90	1	0.901	3
.889	1	0.89	3	0.889	5
.875	1	0.875	br 3	0.877	6
				0.874	5
.845	0.2	0.844	2	0.844	5
.833	0.2	0.830	2	0.829	5
		0.820	2	0.820	8

RATE OF THE OXIDATION REACTION

The reaction was followed by charting the decrease in oxygen pressure with time; the actual results are shown in Figures 4 and 5.

As can be seen from Figure 5, the initial oxygen pressure does not affect the shape of the curves. This is to be expected, since, to use a very simplified mechanism, the concentration of dissolved oxygen in the oxide would vary at most with the square root of the oxygen pressure, assuming oxygen to be in the monatomic form in the dissolved state.

In the case of the run at low oxygen pressure at 830°C, all the oxygen is consumed, whereas with an initial oxygen pressure of 27 cm a limiting pressure of 17 cm is approached asymptotically. This phenomenon does not occur at 940°C and may be explained on the following basis: the oxide layer formed at the lower temperature is less porous, and eventually becomes impervious to oxygen, thus acting like a protective layer.

DISCUSSION OF RESULTS

The fact that the activity remains in the oxide layer during the oxidation indicates that, under the experimental conditions, the mechanism of the reaction is the diffusion of oxygen ions through the oxide layer to the metal-oxide interface. The overall reaction may be described as follows: diffusion of oxygen through the oxide film, reaction of the oxygen with the metal, and also dissolution of the oxygen in the metal to an extent which cannot be ascertained. Hence, it is difficult

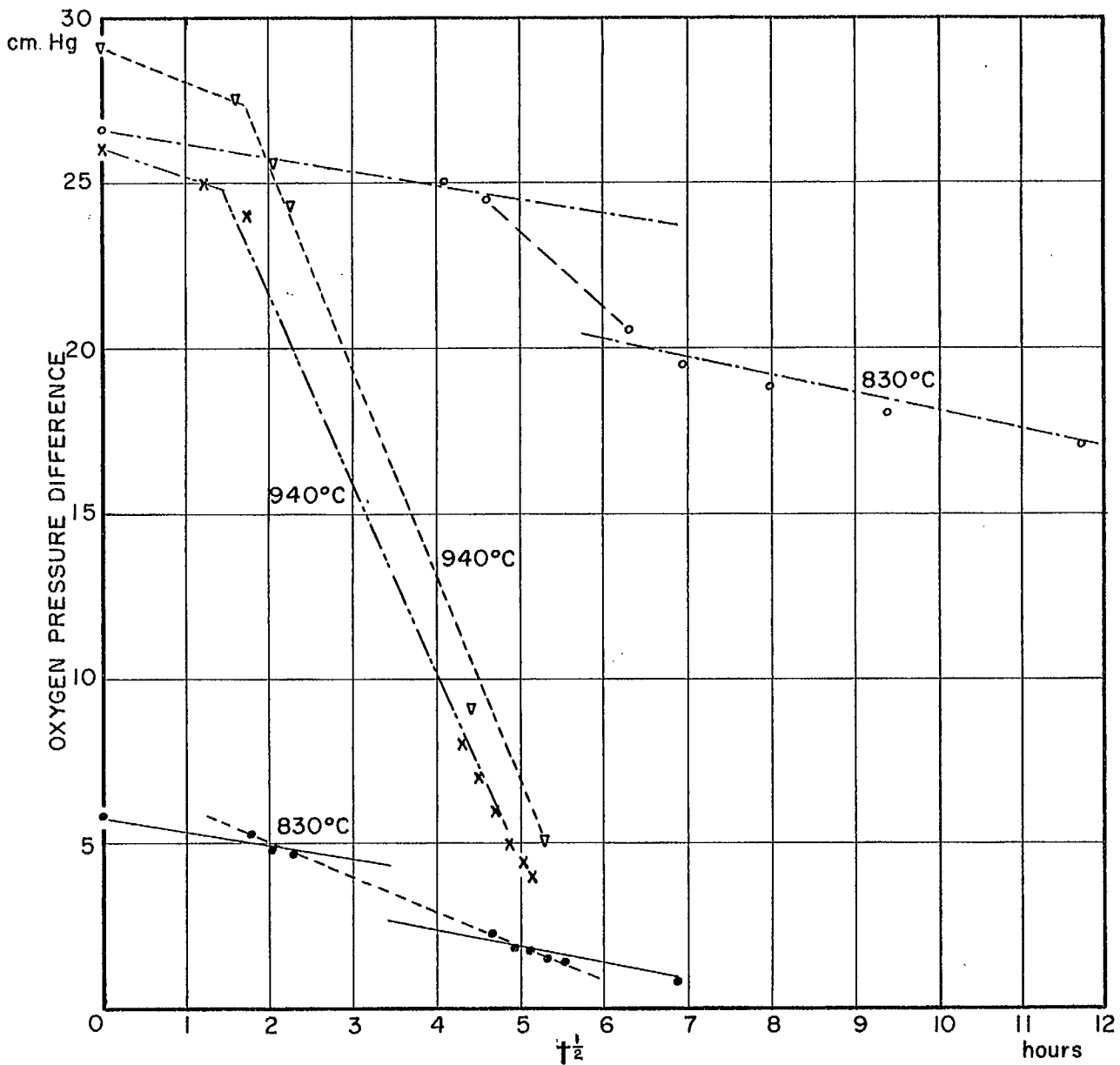


FIG. 4- OXIDATION CURVES OF TITANIUM.

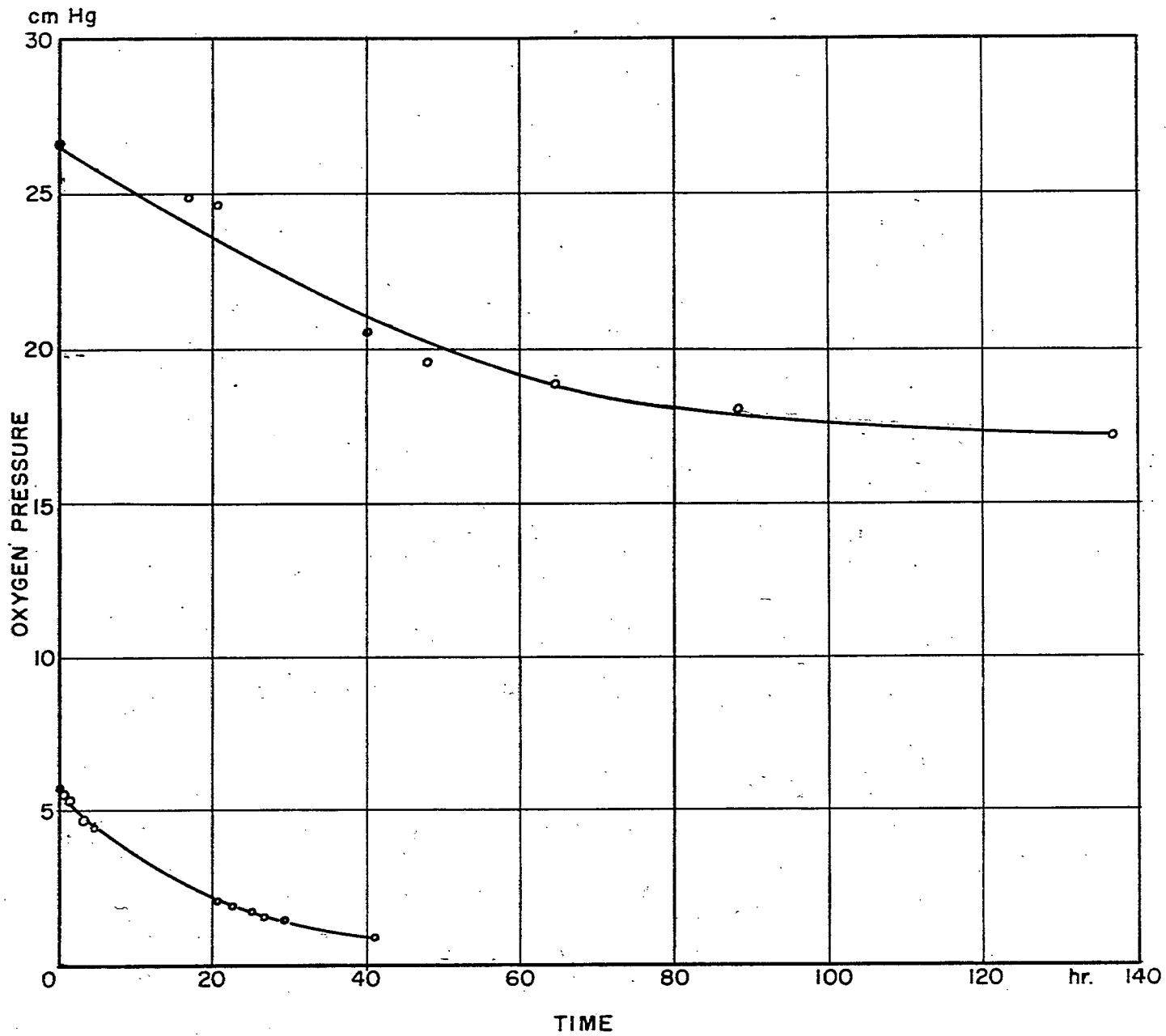


FIG. 5 - OXIDATION CURVES AT 830°C.

to obtain the activation energy for the oxidation reaction itself, as both dissolution and chemical reaction occur together, whatever the method employed to follow the reaction, and furthermore, all the above-mentioned processes proceed with rates which are temperature-dependent. There is also the complicating factor of the phase transition in the metal; the temperature at which this occurs being dependent on the presence of dissolved gases in the metal.*

Under these circumstances, it is most improbable that the plotting of the logarithm of the rate constant for the overall reaction against the reciprocal of the absolute temperature, and multiplying the slope of the line or curve thus obtained, will yield anything that might be called an activation energy for the reaction of titanium with oxygen; both the Arrhenius equation and the absolute reaction rate theory (7) may be validly applied only to experimental conditions that approximate the idealisation under which they are derived. However, as Figures 4 and 5 show, on the whole a parabolic rate law is obeyed in agreement with the results of Richardson and Grant (8).

ACKNOWLEDGMENT

The author is grateful to Dr. G.G. Eichholz for having first suggested this research to him, and for his continued interest and encouragement. He is also indebted to Dr. R. Carter for many informative discussions.

* Note: Since submission of the manuscript in the original form, Thomas and coworkers (9) have published a study of the high-temperature corrosion of Zircalloy in which much the same phenomenon was observed i.e., breaks in the oxidation-time curve.

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