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THE DISSOLUTION AND DIFFUSION OF OXYGEN IN ZIRCONIUM

by

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Chalk River, Ontario

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ABSTRACT

Measurement of the diffusion coefficients of oxygen in α-zirconium by two methods have confirmed the results of Pemsler (for measurements of the dissolution rates of anodic oxides) and the results of Davis (by microhardness measurements on specimens from prolonged thermal oxidation).

Repeated dissolution of anodic films and dissolution of thin thermal films gave higher values for the diffusion coefficient and suggested that this may be a function of the oxygen content.

Oxidation in air gave anomalous microhardness curves showing a much longer 'tail' than expected from the rate of oxygen diffusion. This may be indicative of some interaction between oxygen and nitrogen, with nitrogen diffusing ahead of the oxygen gradient. In the absence of oxygen, the diffusion coefficient for nitrogen is much smaller than that for oxygen.

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1. INTRODUCTION

The diffusion coefficients of oxygen in zirconium determined by Pemsler (1) and Davis, et al. (2) show differences of up to three orders of magnitude at temperatures below 650°C. To investigate the reasons for this discrepancy, both sets of measurements have been repeated under their respective experimental conditions.

2. EXPERIMENTAL

2.1 Materials

Table I shows the principle impurities in the two different batches of crystal-bar zirconium used in the present oxidation studies on pure zirconium. The average grain size of batch 1 was about 0.5 - 1 mm and of batch 2 about 2 - 3 mm in diameter. Specimens of Zircaloy-2 and Zr-3 wt% Al were also used; an analysis for the Zircaloy-2 is given in Table I; no analysis is available for the zirconium-aluminum alloy. The specimens were about 30 x 15 x 3 mm, and were polished mechanically on silicon carbide papers (120 and 400 grit), so that 0.5 - 1 mm from each side of the specimens were removed and finally polished on 6 µm diamond laps. The specimens were then polished chemically in a solution of 39% HNO_3, 57.5% H_2O and 3.5% HF for about 5-10 minutes.

2.2 Procedure

Mechanically and chemically polished zirconium specimens were oxidized either anodically in a saturated solution of ammonium borate of pH 8 at room temperature or thermally in a furnace in oxygen (760 torr) and in air (760 torr) at elevated temperatures. No special precautions were taken to purify either gas.

The reflectivity of the specimen was measured as a function of wave length using a Beckman Spectrophotometer in comparison with an unoxidized specimen as standard. The curves were recorded automatically; typical examples are shown in Fig. 1. From the reflection-minima the thicknesses of the oxide films were calculated for the first three orders using a value of $n = 2$ for the average refractive index of the film (3).

For the determination of diffusion coefficients under the experimental conditions of Pemsler, anodic films were prepared with a standard thickness (710 ± 10 Å) which was confirmed by the Beckman Spectrophotometer. For thermally oxidized specimens the dependence of the minima of reflectivity for the first three orders on temperature and time is shown in Table II.

The time for the film to dissolve in vacuum (10^{-7} torr) at various temperatures was determined optically. A beam of light from a tungsten filament lamp was directed onto the surface of the oxidized specimen (inside the furnace) and reflected onto a CdS photocell. The photocurrent was measured by a Keithley Model 610 electrometer and then recorded. A calibration of the measuring instrument for different oxide film thicknesses was made. After each dissolution experiment the temperature was raised above the dissolution temperature (to 600°C for 30 minutes) to ensure that the oxygen dissolution was complete. For the calculation of the diffusion coefficients the Pemsler analysis (1) was used.

To investigate the experimental conditions used by Davis (2), thermally oxidized specimens were mounted on edge in bakelite, ground down approximately 2-3 mm, then mechanically and chemically polished. The oxygen gradients in the metal were determined by microhardness measurements made with a Tukon-Tester designed for the determination of Knoop and 136°C diamond pyramid hardness numbers using 50, 100 and 200 g loads. The results are the average of 3-4 traverses made on each specimen at different points (Fig. 2). Diffusion coefficients were calculated in two ways; firstly, from the depth of penetration (taken at the minimum in the microhardness traverse), and secondly, from the slope of the steep part of the curve.*

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*The very high hardness values (>3000 KHN) close to the surface were ignored as they were thought to arise from the indenter catching on a step produced at the metal-oxide interface during etching. In some instances these hardness values were higher than that estimated for diamond (8).

Individual readings were reproducible within 20%. The diffusion coefficients were calculated using the analysis of Davis.

3. RESULTS

3.1 Dissolution of Anodic Oxides

The rates of decrease of thickness of anodic oxide films (initially 710 ± 10 Å) in vacuum (10^{-7} torr) as a function of time at 450°C, 480°C and 550°C are shown in Fig. 3. Diffusion coefficients calculated from the linear part of these curves are shown in Fig. 4 and are compared with diffusion coefficients calculated from the time after which the whole oxide layer disappeared (points a, b and c in Fig. 3). For ease of experimentation, the second method of estimating oxide dissolution was used subsequently.

Repeated growth and dissolution of an anodic oxide on the same specimen under the same experimental conditions showed that the average dissolution rate of the oxide film is higher on the second and subsequent occasions than initially. On repetition, however, relatively smaller increases in the dissolution rate were observed (Fig. 5). The diffusion coefficients at 600°C generally lie below the straight line through the other points. This may represent a systematic error introduced by the method of calculating the coefficients from the time taken for the oxide to dissolve completely.

3.2 Dissolution of Thermal Oxides

Dissolution of oxide films thermally formed on zirconium at 400°C to thicknesses approximately the same as the standard anodic film thickness was observed to be more rapid than that of the anodic oxide (Fig. 6). A specimen was oxidized in oxygen at 400°C for 1, 2 and 3 hours and the thicknesses of the oxide layers determined by using the Beckman spectrophotometer. One part of the reflectivity curves is indicated by Fig. 7. The specimen was then annealed under vacuum (10^{-7} torr) at the same formation temperature for 216 hours to dissolve the oxide layer. Curve 4 in Fig. 7 shows the result. No decrease of the oxide film thickness could be found; taking the diffusion coefficient of 1.6×10^{-16} cm^2/sec for 400°C by extrapolating the middle line in Fig. 4, a decrease of the oxide thickness of 130 Å would be expected, giving the reflectivity minimum at the wave length shown in Fig. 7

3.3 Microhardness Measurements

The microhardness curves were found to pass through a minimum at the point where the gradient meets the interior of the specimen (which showed a nearly constant hardness). These minima were used as the penetration distance of oxygen into the metal for calculating the diffusion coefficients; a second figure for this coefficient was obtained from the slope of the steep part of the gradient.

Results of measurements on specimens oxidized in oxygen (or air) at 500-800°C are presented in Table III and Fig. 8, in comparison with the other published results (1, 2, 4, 6, 7). Figures 9 and 10 show the hardness gradients in the metal for specimens oxidized at 600°C in air and oxygen respectively from which the diffusion coefficients were calculated.

Pure zirconium, Zircaloy-2 and Zr-3 wt% Al specimens were oxidized at 600°C for 22 hours and the oxygen gradients measured (Fig. 11). These results were confirmed by a repeat experiment. Another zirconium specimen was cut like a wedge and, after polishing, oxidized at 800°C for 24 hours. After this time, the edges and the thinnest part of the metal wedge (thickness <500 μm) were covered by white oxide layers. Other parts of the wedge showed only a black oxide layer. Microhardness measurements showed that the oxygen gradients had already met in the part where the white oxide layer was formed (Fig. 12); a repeat confirmed this observation.

Figure 13 shows the microhardness traverses observed after the oxidation of specimens in air and subsequent annealing in vacuum. A zirconium specimen was oxidized for 22 hours in air at 700°C; it was then cut in two pieces. One part was annealed under vacuum (10^{-7} torr) at the same temperature of 700°C for 1250 hours. The result shows that the shape of the gradient has not changed markedly and the black oxide layer was still there. The other part of the specimen was annealed at 800°C for 70 hours also under vacuum (10^{-7} torr). The oxide had dissolved, but most of the oxygen remained near the original surface, and the results can be compared with a microhardness curve for another specimen oxidized for 22 hours in air at 800°C.

4. DISCUSSION

Good agreement was obtained with the results of Pemsler by using his experimental conditions and method of analysis. Variations in the experimental method, however, changed the apparent diffusion rate of oxygen into the metal. Good agreement was also obtained with the results of Davis on specimens oxidized in oxygen using similar experimental conditions and his method of analysis. The diffusion coefficients after oxidation in air, calculated from the minimum in the hardness curve, were higher even than those reported by Davis. Coefficients calculated from the slope of the steep part of the gradient were in good agreement with other published data.

With increasing time of oxidation in air, the diffusion coefficient (calculated from the minimum in the hardness curve) decreases, since there was relatively little change in the position of the minimum (Fig. 9). There was little change in the slope of the gradient and the whole gradient apparently moved into the specimen. Microhardness gradients which do not change with exposure time are a natural corollary of linear oxidation and have been observed by Wallwork and Jenkins (5).

The hardness gradients formed during oxidation in air show two prominent regions of different slope, whereas in oxygen only one slope was observed. The steeper portion of the gradient in air gives diffusion coefficients comparable to those for oxygen and may represent diffusion of oxygen from the air. The part of the gradient with the lower slope may be due to some other species diffusing more rapidly than oxygen. Nitrogen on its own diffuses more slowly than oxygen, but it may be that when both species are present, there is an interaction which results in the nitrogen diffusing more rapidly. Probst, Evans and Baldwin (4) found a complicated interaction between nitrogen and oxygen when exposure was changed from one to another of the three media employed (oxygen, nitrogen and air).

The results of Fig. 11 may indicate that with increasing hardness of the metal interior in the series zirconium (91 KHN) Zircaloy-2 (180 KHN) and Zr-3 wt% Al (360 KHN) the penetration of the hardness gradient measured by the minimum in the hardness curve becomes larger. The thicknesses of the oxide layers were approximately 10, 30 and 300 µm for zirconium, Zircaloy-2 and Zr-3 wt% Al respectively, and if the diffusion rates are the same for these alloys, one would expect a decrease in the thickness of the diffusion zone with increasing oxidation rate.

In the case of the wedge-shaped specimen, the oxygen appeared to have diffused into the metal faster in the thinner parts of the specimen. This may be the result either of an interaction between the two gradients or of the stresses resulting from the oxidation. The occurrence of white oxide may be a consequence rather than a cause of these effects.

The results presented here cannot be explained by a simple analysis of the diffusion process using a single diffusion coefficient at each temperature. Thus, the rate of diffusion of oxygen apparently increases with increasing oxygen content of the metal (and perhaps the content of other impurities) as shown by:

a. Effect of re-anodizing specimens.

b. Effect of presence of dissolved oxygen initially (thermally formed films).

A simple analysis would predict slower solution of the film in the second instance. However, the dissolution of oxygen in the lattice causes an expansion which may permit easier movement of oxygen between adjacent interstitial positions. Thus, although the number of empty interstitial positions decreases with increasing oxygen content, the increased jump frequency may more than balance this, giving a net increase in diffusion coefficient with increasing oxygen content. Stresses set up as a result of the oxygen gradient may also assist this process (e.g. by multiplication of dislocations). Stressing of the metal by the presence of the oxide film may also influence this process, and thus the nature of the oxide and its rate of growth may influence the diffusion by mechanisms other than mere consumption of oxygen saturated metal.

5. CONCLUSION

The diffusion coefficients for oxygen in zirconium calculated from the rate of dissolution of anodic oxide films by Pemsler have been confirmed.

However, the diffusion coefficient appears to be a function of the oxygen content of the metal (e.g. on repeated dissolution of anodic films or dissolution of thin thermally formed oxides). For prolonged thermal oxidation, where measurable dissolved oxygen gradients are present at the metal-oxide interface, the measured diffusion coefficients are higher, and are approximately in agreement with those of Davis and Béranger.

During oxidation in air, there is apparently some interaction between the diffusing species present (probably oxygen and nitrogen) which results in anomalies in the micro-hardness gradients, and hence in the diffusion coefficients calculated from the depth of penetration alone.

6. REFERENCES

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TABLE I

IMPURITY CONTENT OF ZIRCONIUM AND ZIRCALOY-2 SPECIMENS IN WT%

Impurities	Zirconium Batch 1 (large grain size)	Zirconium Batch 2 (small grain size)	Zircaloy-2
Al	0.0025	0.005	0.004
Mn	0.001	0.005	0.001
Si	0.006	0.005	0.007
Cr	0.001	0.005	0.09
Mg	0.001	0.005	0.001
Fe	0.015	0.005	0.14
Ni	0.001	0.005	0.05
Cu	0.0025	0.001	0.002
Hf	0.006	0.007	0.006
O	0.016	0.03	0.1
C	---	---	0.008
Ta	---	---	0.02
Ti	---	---	0.002
Sn	---	---	1.45

TABLE II

VARIATION OF THE WAVE LENGTH OF MINIMUM REFLECTIVITY WITH TIME AND TEMPERATURE OF THERMALLY OXIDIZED SPECIMENS

Zirconium	Oxidation Temperature (°C)	Exposure Time (hrs)	Minima of Reflectivity (μm)	Order of Interference
Batch 1, Table 1	300	1	310	1
" "	400	1	1200 410 262	1 2 3
		2	1300 450 300	1 2 3
		3	1375 485 310	1 2 3
" "	500	1	2100 925 540	1 2 3
		2	1225 725	2 3
		3	1275 825	2 3
" "	600	1	1650	3

TABLE III

DIFFUSION COEFFICIENTS FOR OXYGEN IN ZIRCONIUM

(AFTER THE ANALYSIS OF DAVIS, ET AL.)

Temp. (°C)	Time (sec)	Distance of Microhardness Minimum from Interface (μm)	Atmosphere	Diffusion Coefficient (cm^2 sec^{-1}) (1)	(2)
600	$7.9x10^4$	60	Air 760 torr	$3.1x10^{-11}$	$3.1x10^{-12}$
600	$6.0x10^5$	90	"	$1.0x10^{-11}$	$1.2x10^{-12}$
600	$3.4x10^5$	80	"	$1.4x10^{-11}$	$1.3x10^{-12}$
700	$7.9x10^4$	110	"	$1.1x10^{-10}$	$4.0x10^{-11}$
800	$8.3x10^4$	170	"	$2.6x10^{-10}$	$2.3x10^{-10}$
550	$3.1x10^5$	25	Oxygen 760 torr	$1.5x10^{-12}$	$1.3x10^{-12}$
600	$7.8x10^5$	35	"	$5.0x10^{-12}$	$3.9x10^{-12}$
600	$3.0x10^5$	40	"	$4.0x10^{-12}$	$3.9x10^{-12}$
680	$8.5x10^4$	50	"	$2.2x10^{-11}$	$1.8x10^{-11}$
680	$1.0x10^5$	60	"	$2.7x10^{-11}$	$1.9x10^{-11}$

(1) Calculated from minimum in microhardness plot

(2) Calculated from initial slope of microhardness plot

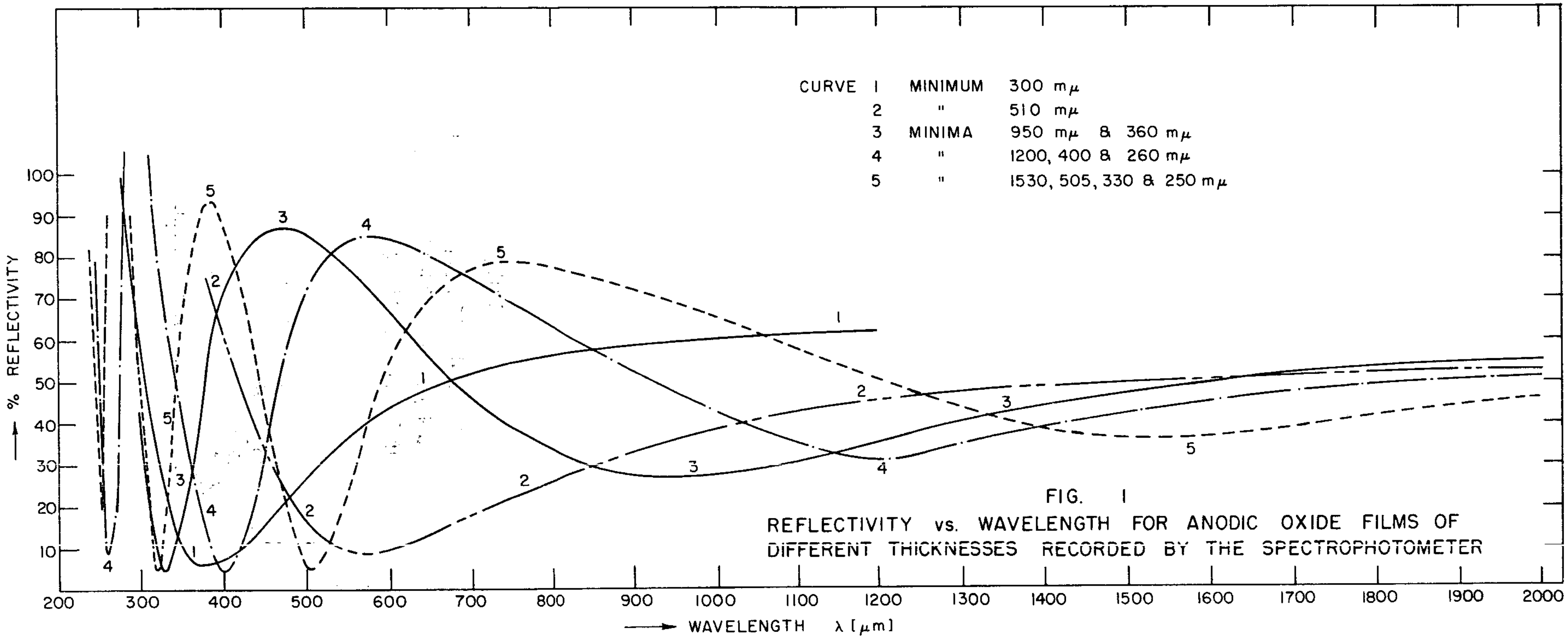

FIG. 1

REFLECTIVITY vs. WAVELENGTH FOR ANODIC OXIDE FILMS OF DIFFERENT THICKNESSES RECORDED BY THE SPECTROPHOTOMETER

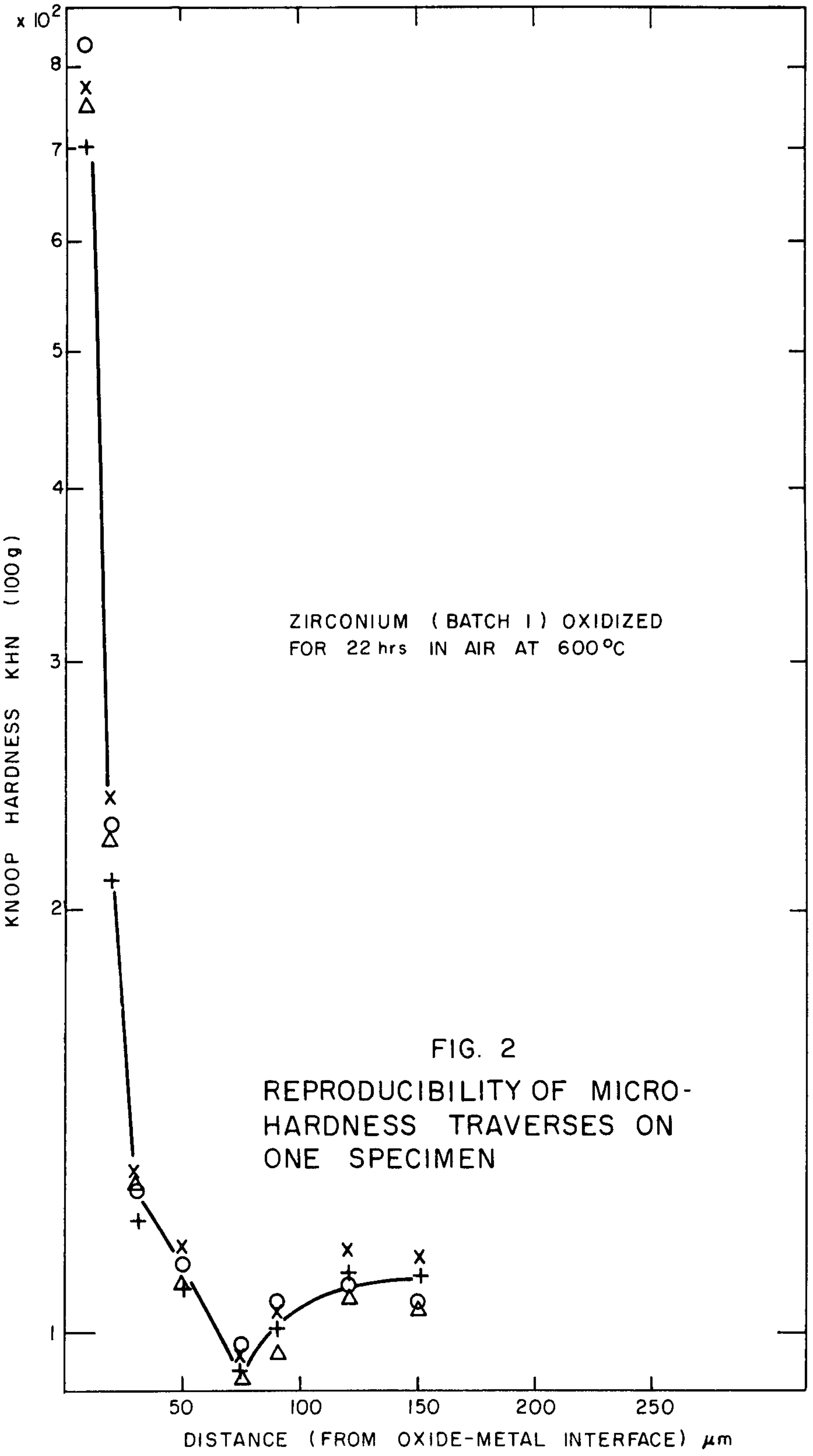

FIG. 2

REPRODUCIBILITY OF MICRO-HARDNESS TRAVERSES ON ONE SPECIMEN

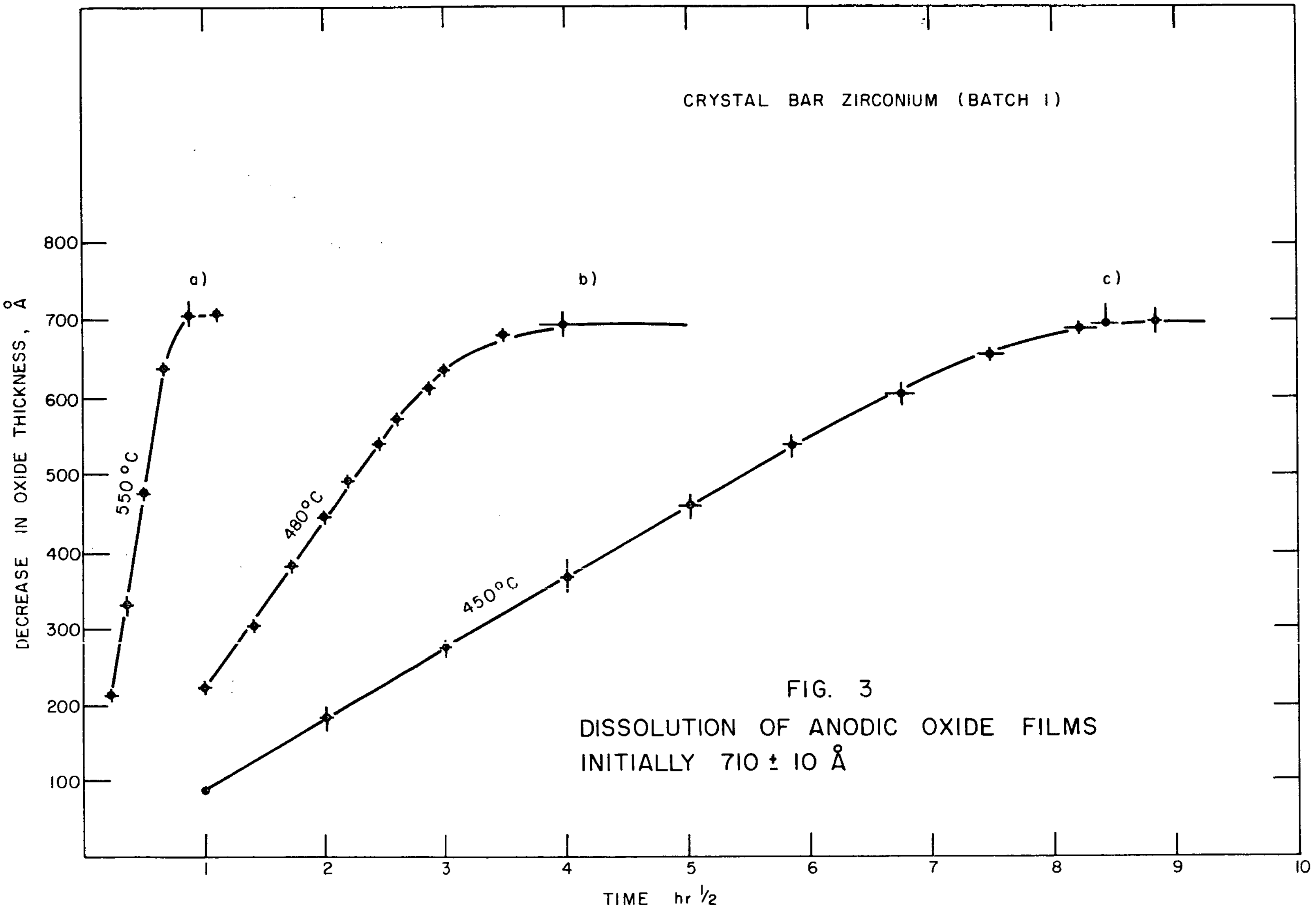

FIG. 3

DISSOLUTION OF ANODIC OXIDE FILMS INITIALLY 710 ± 10 Å

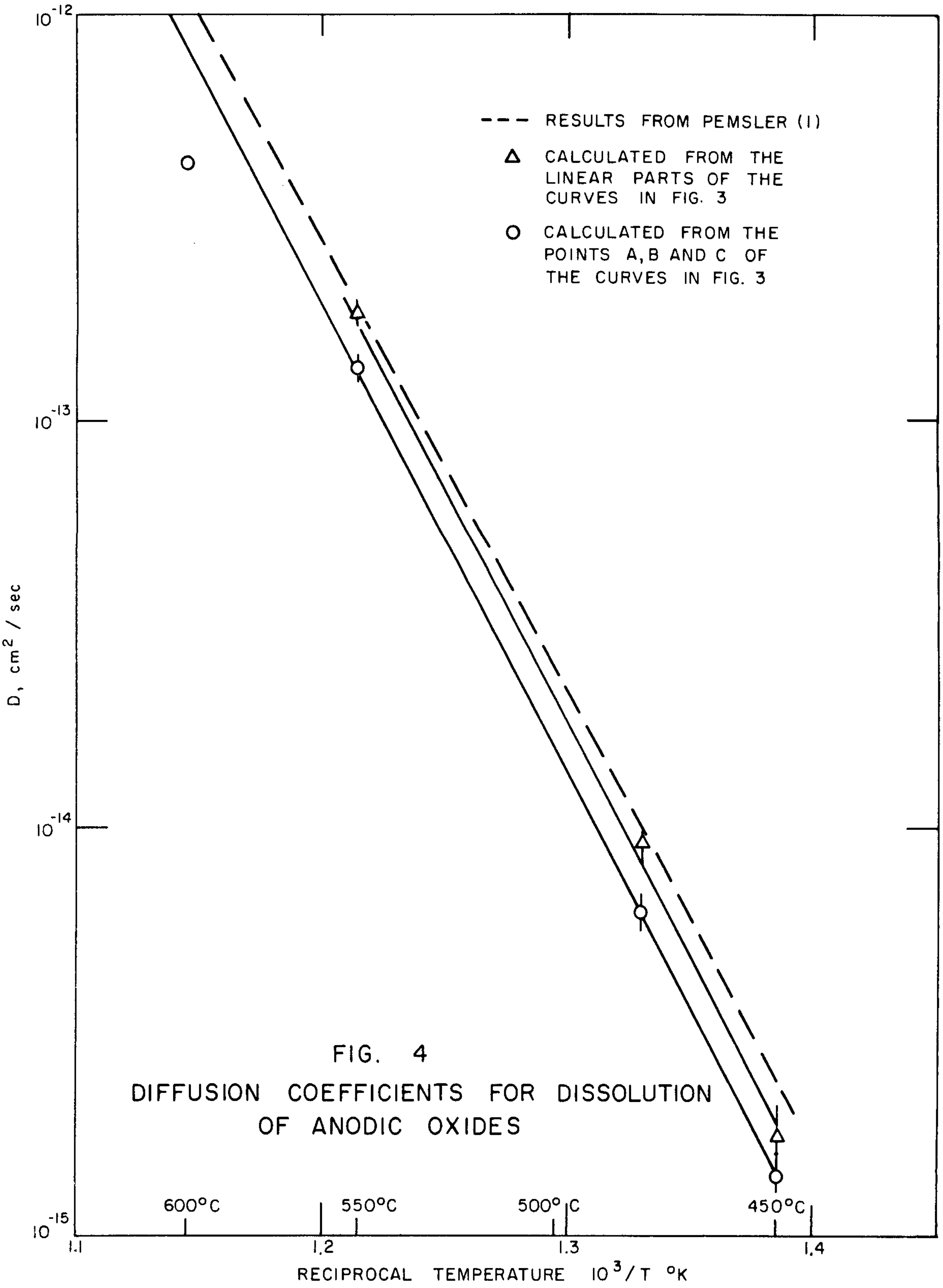

FIG. 4

DIFFUSION COEFFICIENTS FOR DISSOLUTION OF ANODIC OXIDES

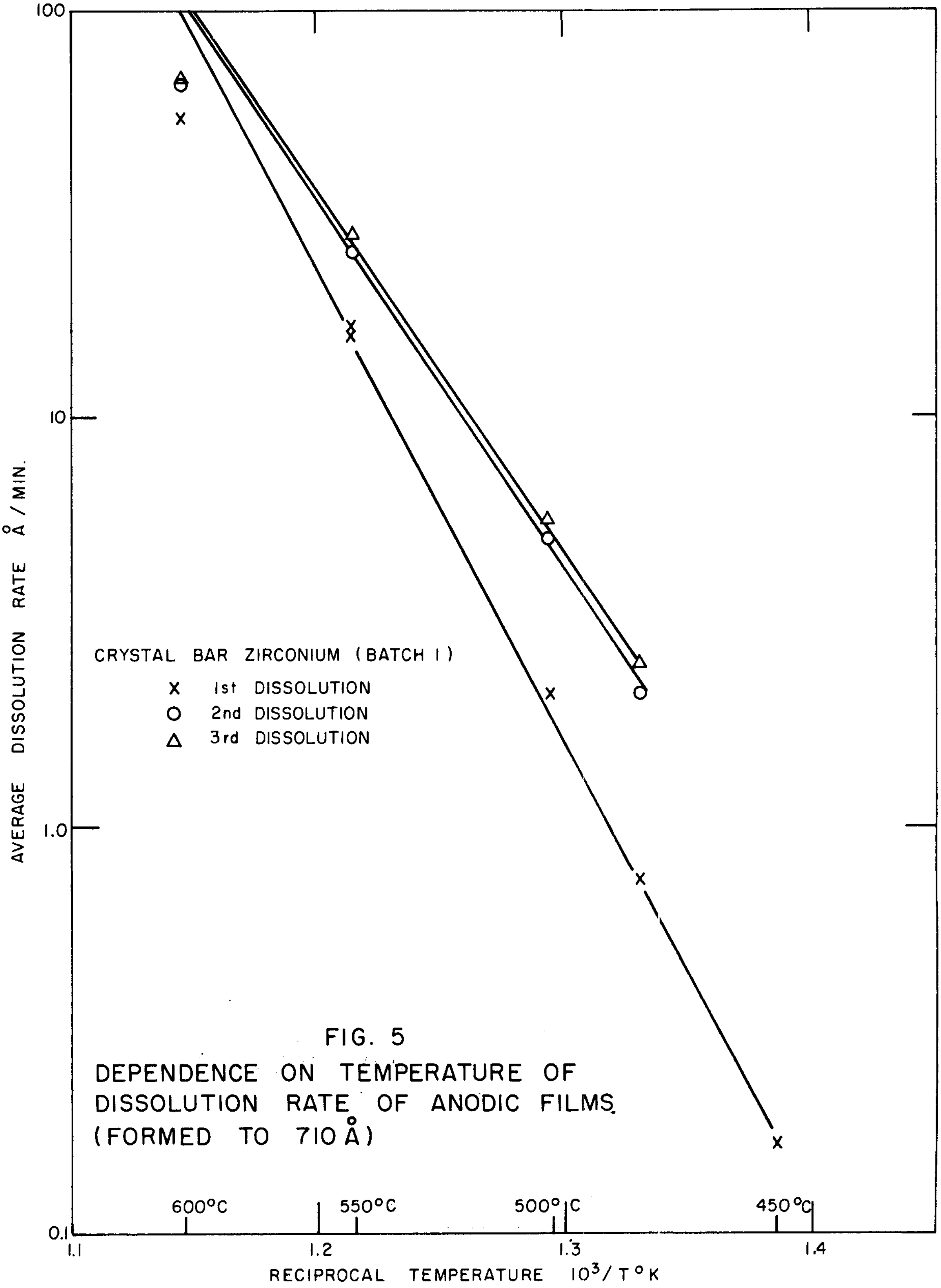

FIG. 5

DEPENDENCE ON TEMPERATURE OF DISSOLUTION RATE OF ANODIC FILMS (FORMED TO 710 Å)

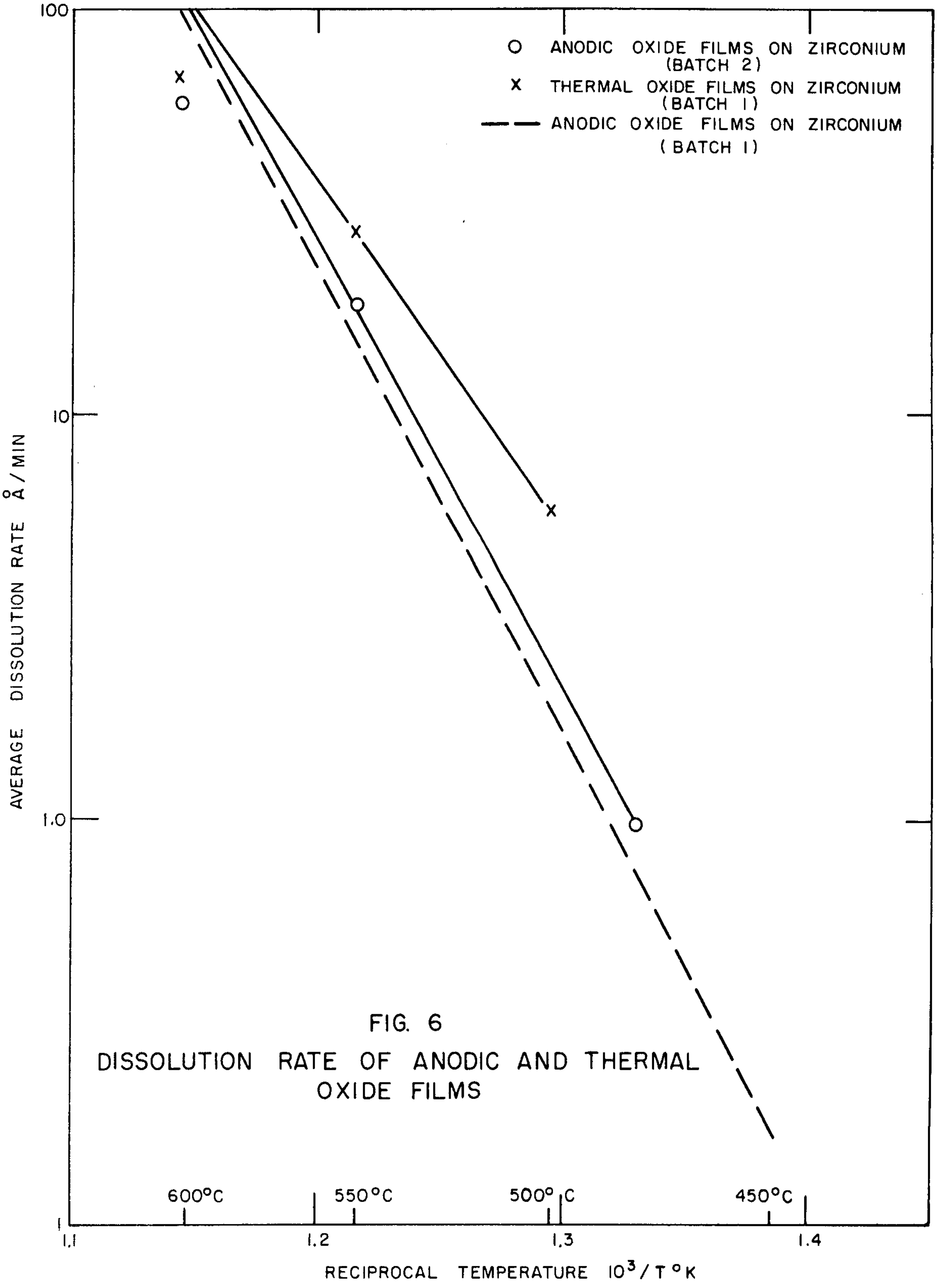

FIG. 6

DISSOLUTION RATE OF ANODIC AND THERMAL OXIDE FILMS

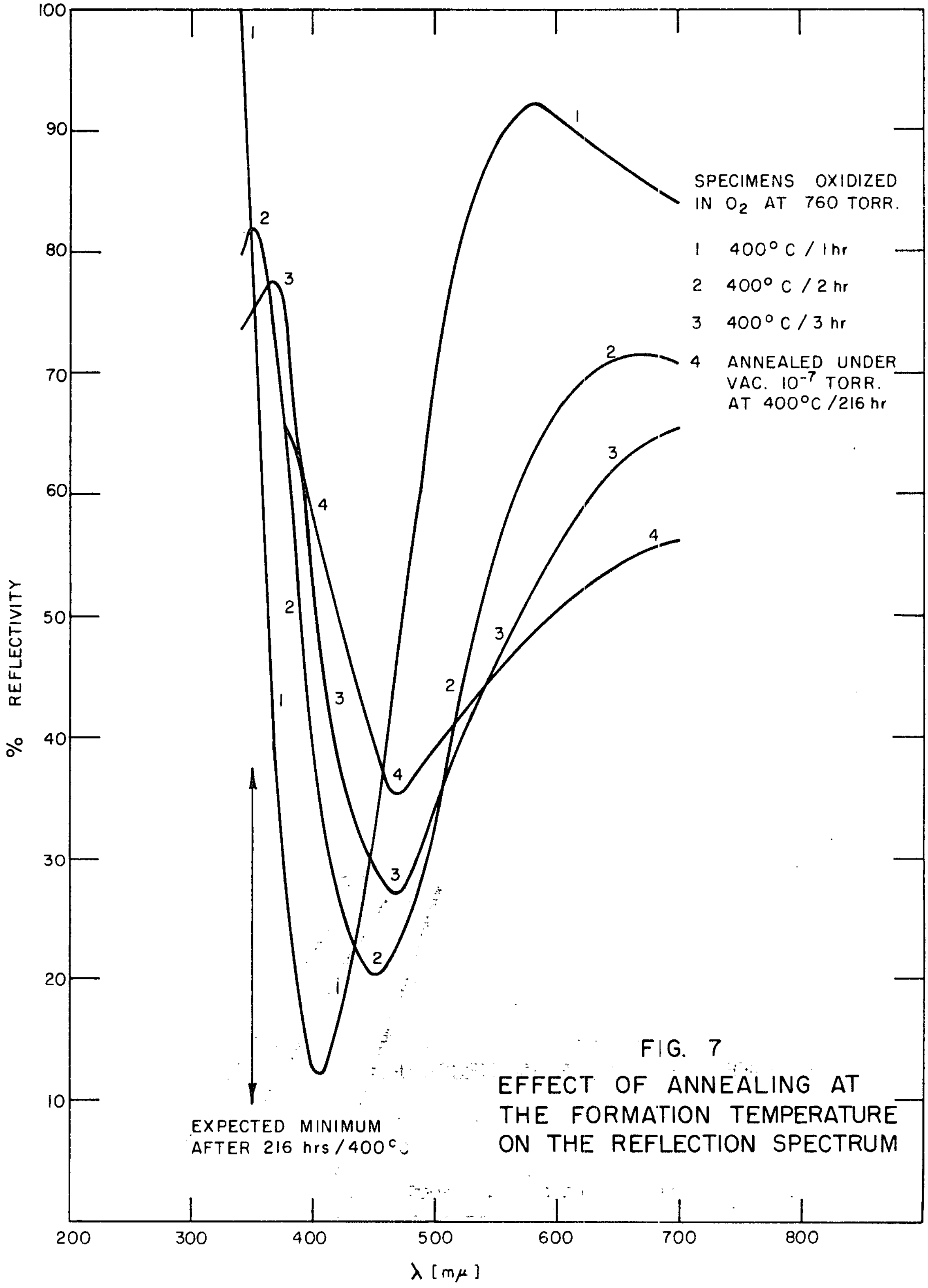

FIG. 7

EFFECT OF ANNEALING AT THE FORMATION TEMPERATURE ON THE REFLECTION SPECTRUM

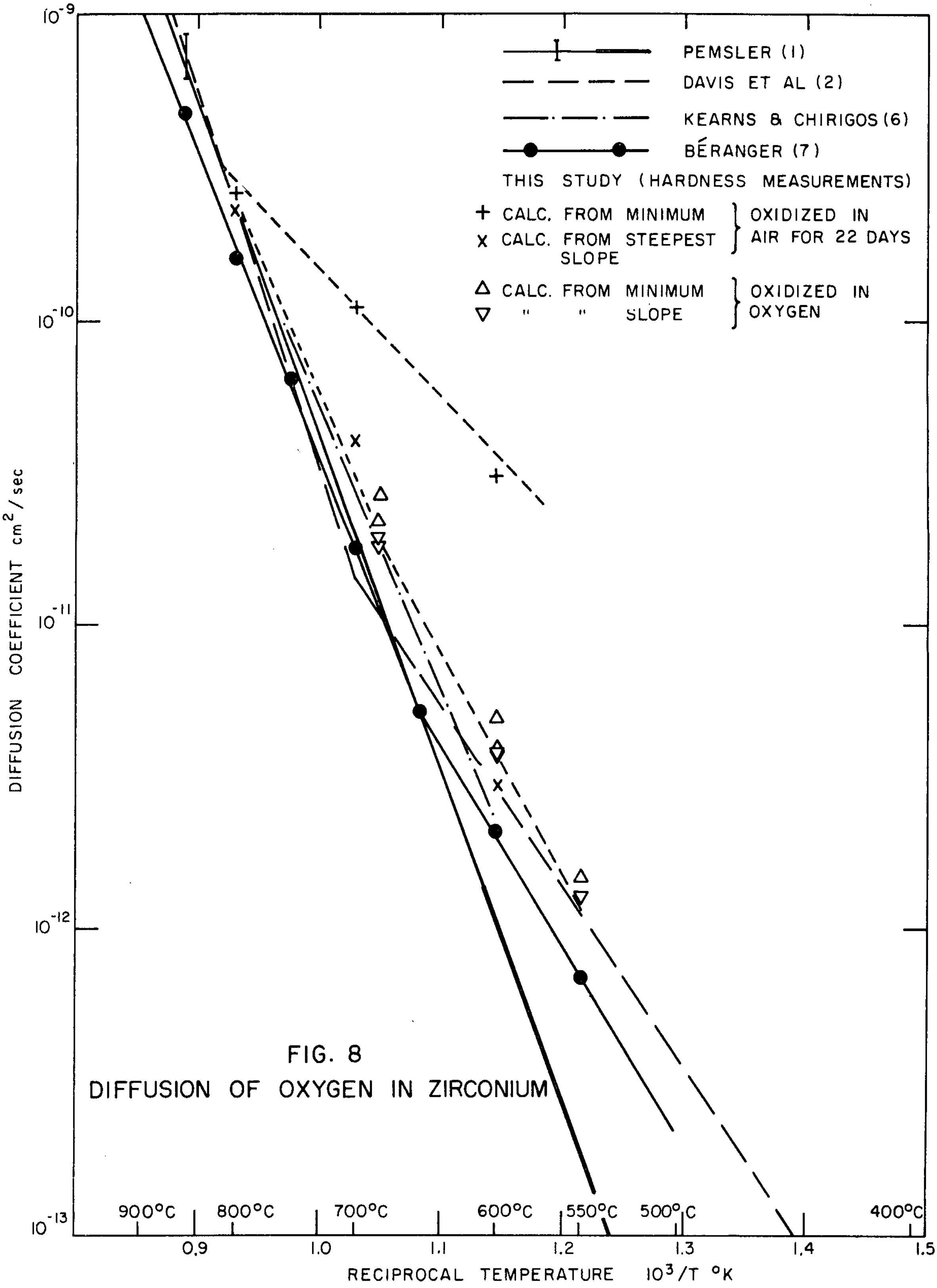

FIG. 8
DIFFUSION OF OXYGEN IN ZIRCONIUM

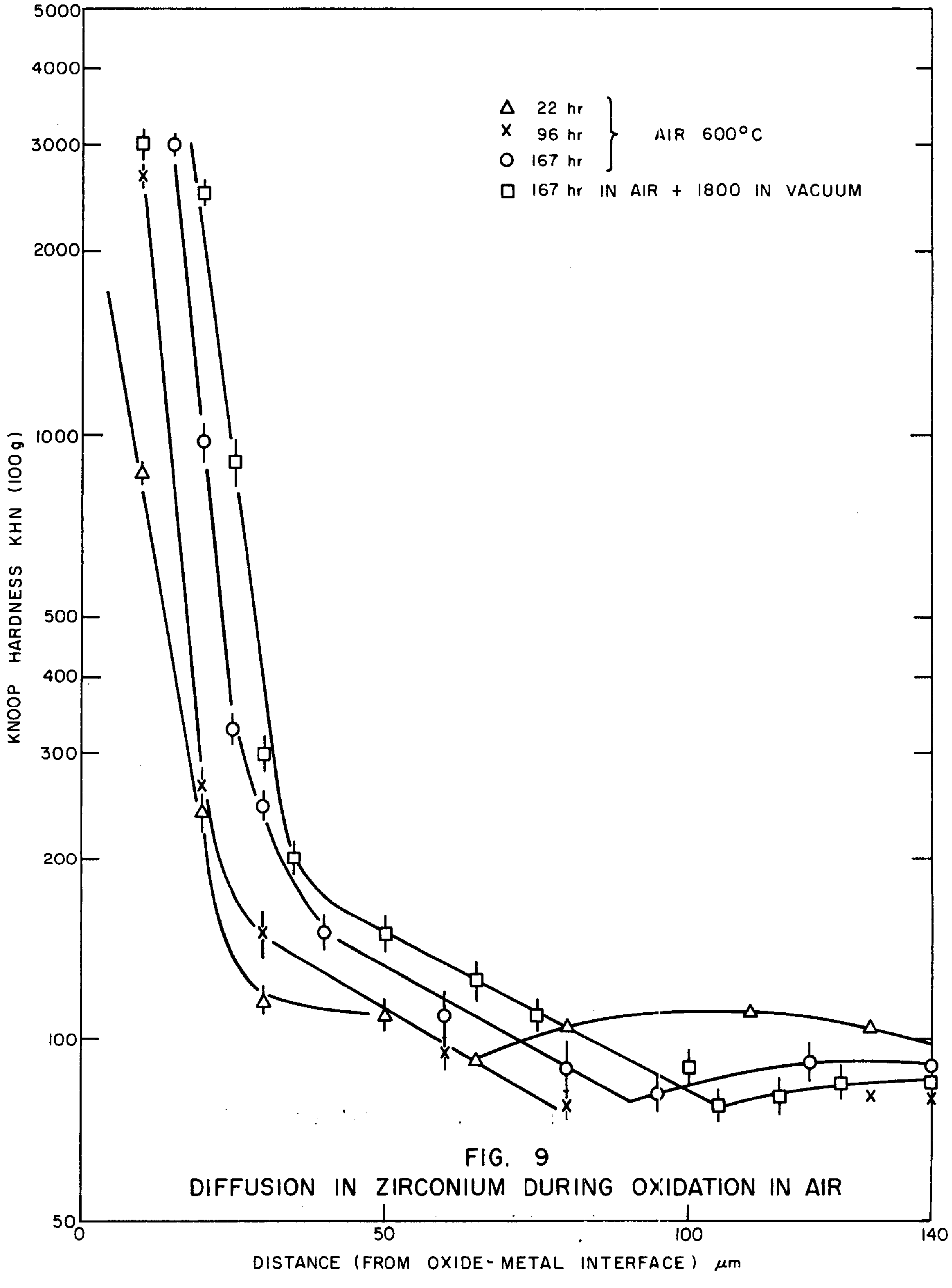

FIG. 9
DIFFUSION IN ZIRCONIUM DURING OXIDATION IN AIR

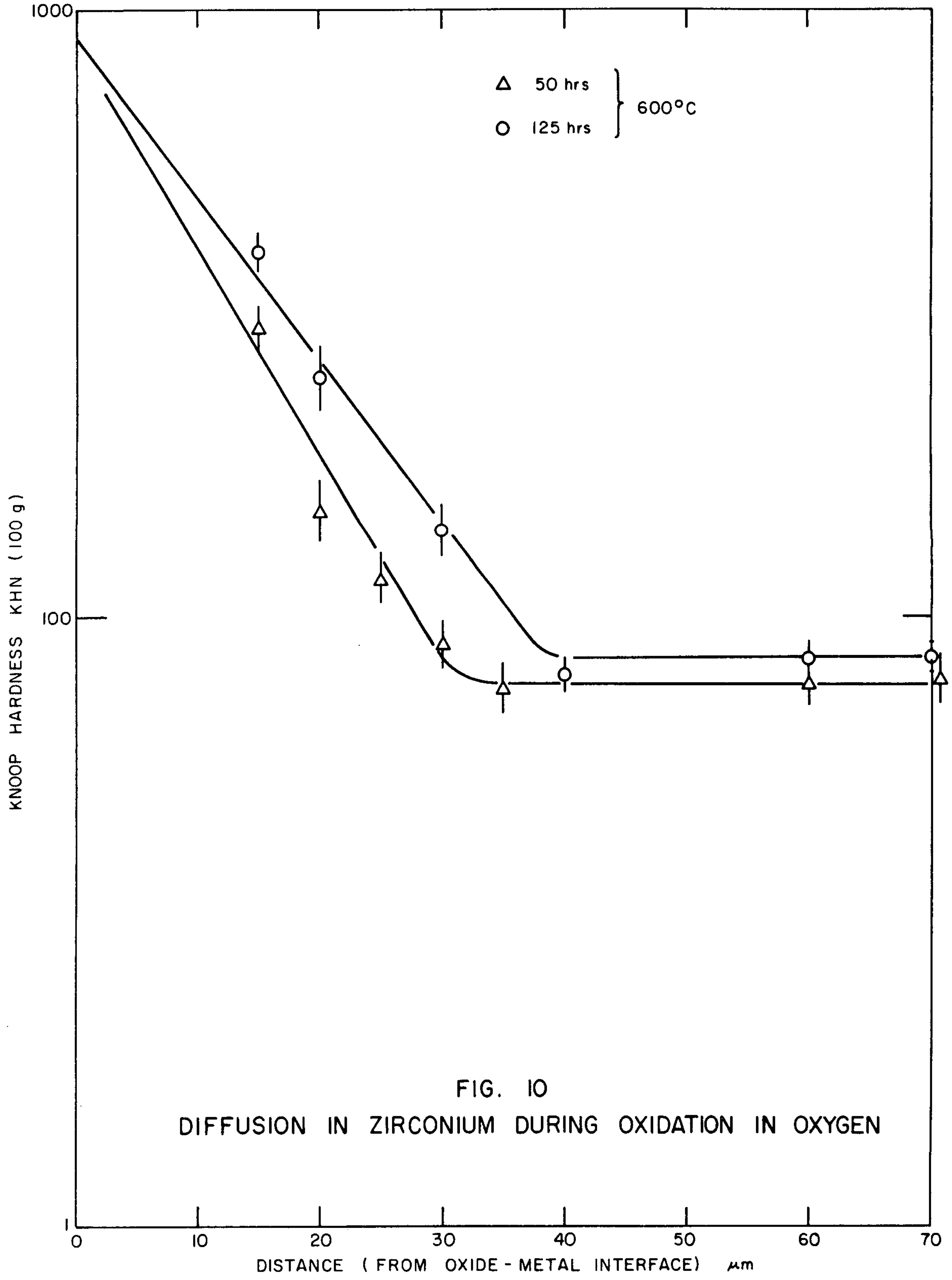

FIG. 10

DIFFUSION IN ZIRCONIUM DURING OXIDATION IN OXYGEN

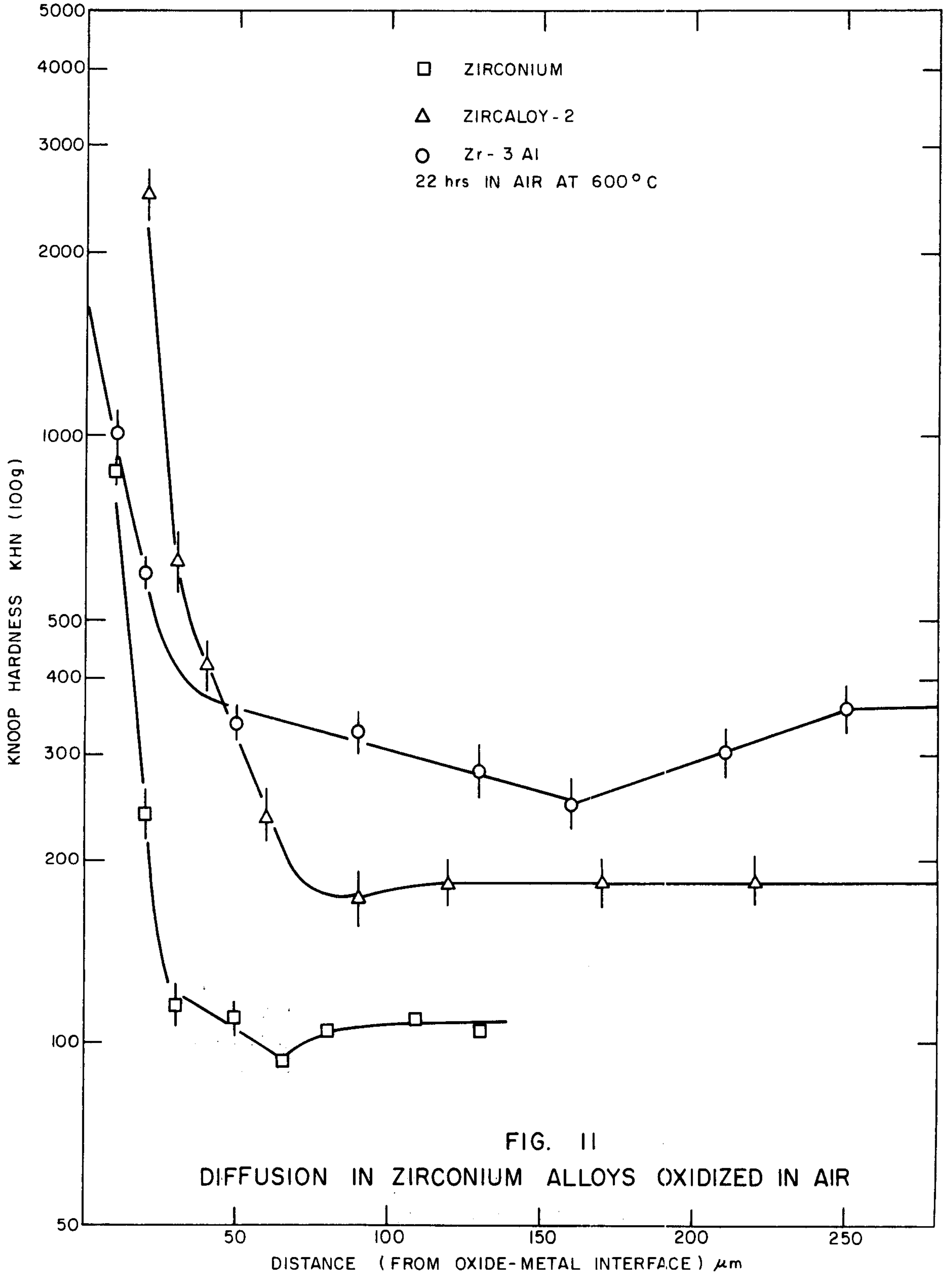

FIG. 11

DIFFUSION IN ZIRCONIUM ALLOYS OXIDIZED IN AIR

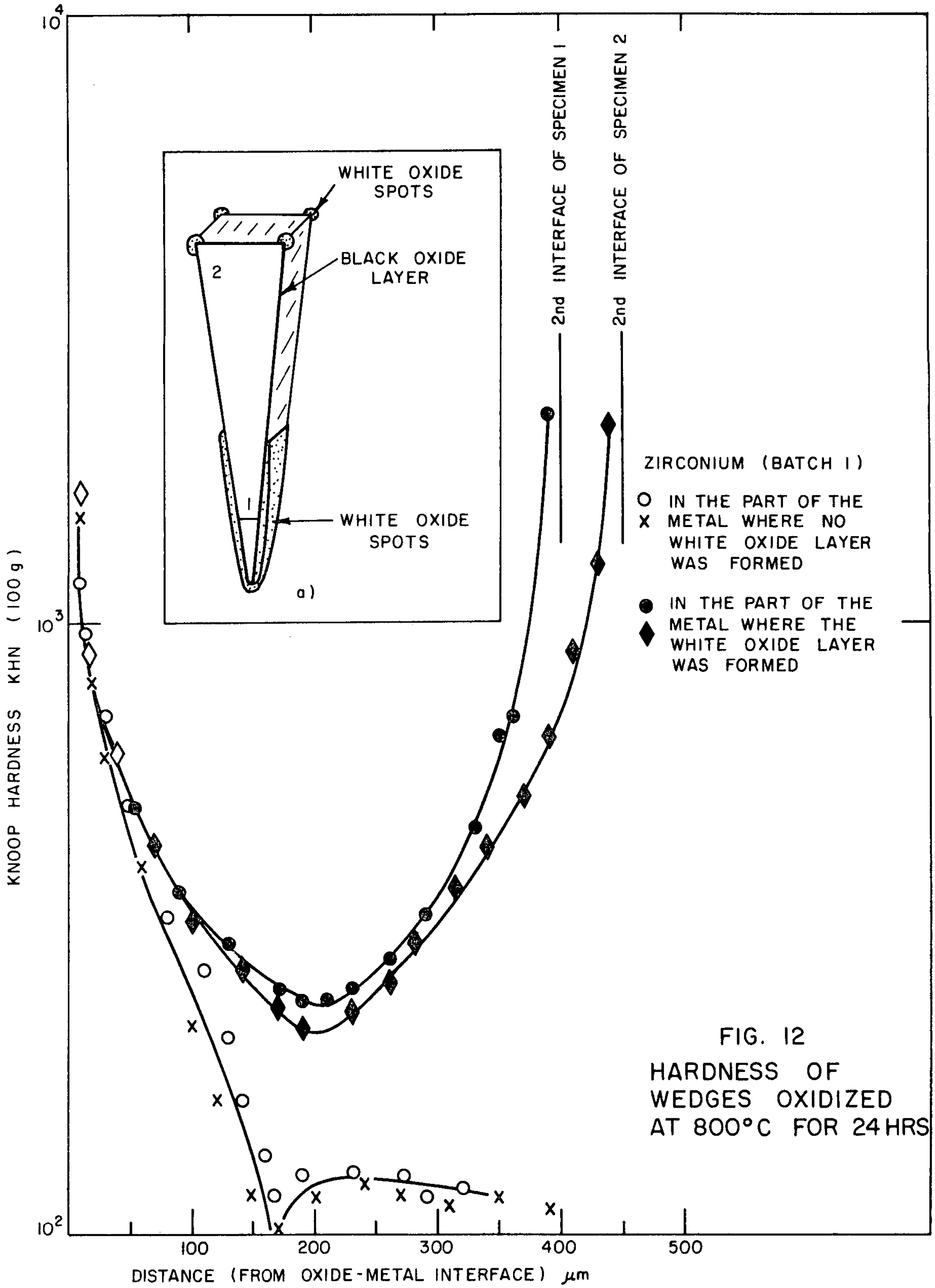

FIG. 12

HARDNESS OF WEDGES OXIDIZED AT 800°C FOR 24 HRS

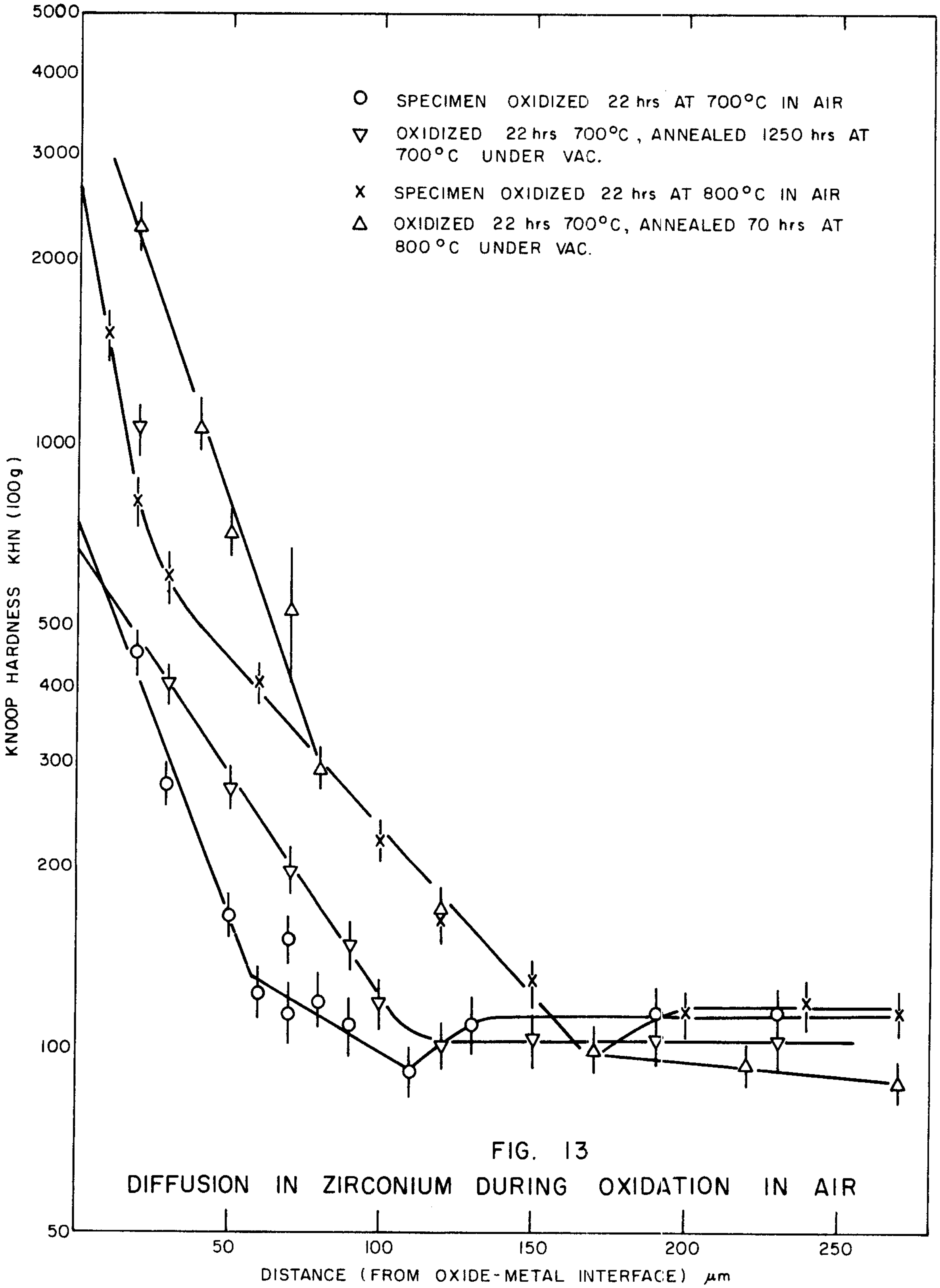

FIG. 13

DIFFUSION IN ZIRCONIUM DURING OXIDATION IN AIR