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An Investigation Of
SCALING OF ZIRCONIUM AT ELEVATED TEMPERATURES

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By

H. B. Probst

E. B. Evans

W. H. Baldwin, Jr.

Conducted By

Department of Metallurgical Engineering
Case Institute of Technology

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Current Work

During the last quarter single crystals of iodide zirconium were oxidized in an effort to determine any lattice relationship existing between zirconium and the oxide overlay. In the early stages of oxidation a single crystal of the oxide formed on a single crystal of zirconium. With continued oxidation the oxide single crystal degenerated to a polycrystalline structure. This degeneration occurred before the oxide had grown to sufficient thickness to allow orientation determinations by the back-reflection Laue method. Glancing techniques may prove to be fruitful in determining the oxide orientation before it becomes polycrystalline.

A comprehensive review of experimental data and proposed theories to explain the oxidation behavior of zirconium has been made. This review suggests the possibility that growth of zirconium in air and oxygen occurs by two distinctly different mechanisms. Also, the possibility of zirconium ions diffusing outwardly through the scale above 1000°C , thus explaining the absence of high-temperature growth, again appears feasible. Experimental work is now in progress to clarify these points. The results of this work will be reported in the next report.

Studies of the diffusion of oxygen and nitrogen in zirconium during scaling have also been made during the last quarter. These results are reported below.

Diffusion Studies

During high temperature scaling of zirconium in oxygen or nitrogen the reacting gas is distributed between the scale and the metal. Below 862°C (the alpha-beta transformation temperature), oxygen or nitrogen diffuses in alpha-zirconium, the diffusing gas being supplied by the scale overlay. The depth of contamination cannot be measured metallographically with any definiteness. Above 862°C , however, oxygen or nitrogen diffuses in beta-zirconium, resulting in the development of the alpha-zone at the scale-metal interface, Fig. 1. On cooling, the alpha-zone is readily outlined between the scale and the transformed-beta phase after metallographic polishing and etching.

From measurements of the depth of the outlined alpha zone it is possible to calculate not only the amount of gas dissolving in the metal but the diffusion rate in alpha-zirconium as well. The amount of dissolved gas subtracted from the total weight-gain in the scaling reaction yields the amount of gas contributing to scale formation, from which the rate of metal consumption may be calculated. These calculations were made for the temperature range $900^{\circ}\text{-}1200^{\circ}\text{C}$, employing available specimens of various grades of zirconium which had been scaled in air, oxygen, and nitrogen. The rate of metal consumption at lower temperatures was estimated from solutions to the diffusion equation.

Depth of Contamination

The dissolution of gas in iodide zirconium above 862°C follows a parabolic rate law, as suggested by the straight lines obtained in plots of the square of the depth of the alpha-diffusion zone versus scaling time. The slopes of these plots, i.e., the rates of movement (k) of the alpha-diffusion zone, are listed in Table I for runs in air, oxygen, and nitrogen.* The values for the air-runs are the same as those for the oxygen-runs, indicating that oxygen is the major diffusing gas in air-scaling.

These data were utilized in determining the diffusion coefficients of oxygen and nitrogen in alpha zirconium assuming that

$$X_{\alpha}^2 = 4\gamma^2 D_{\alpha} t = kt \quad (I)$$

where

X_{α} = depth of alpha-diffusion zone, cm.

γ = dimensionless parameter

D_{α} = diffusion coefficient in alpha-zirconium, cm² per sec.

t = time, sec.

k = rate of movement of alpha-diffusion zone, cm² per sec.

The solution for γ in the present moving-boundary problem is available (1) and is given by

*The k-values are only valid for estimating the depth of contamination for scaling times less than those required for breakaway. After breakaway, the depth of the alpha-zone appears to be about the same as that existing immediately before breakaway.

$$C_{II,I} - C_{I,II} = \frac{(C_S - C_{II,I})e^{-\delta^2}}{\delta\sqrt{\pi}\operatorname{erf}\delta} - \frac{(C_{I,II} - C_0)e^{-\delta^2}}{\delta\sqrt{\pi}\beta[1-\operatorname{erf}(\delta\sqrt{\beta})]} \quad (II)$$

where

C_S = concentration of the diffusing gas in alpha-zirconium at the scale-metal interface, i.e., maximum solubility.

$C_{II,I}$ = concentration of the diffusing gas in alpha-zirconium at the alpha-beta interface. This is the concentration obtained from the phase diagram at the boundary between the alpha and alpha + beta fields at a given temperature.

$C_{I,II}$ = concentration of the diffusing gas in beta zirconium at the alpha-beta interface. This is the concentration obtained from the phase diagram at the boundary between the beta and alpha + beta fields at a given temperature.

C_0 = initial concentration (assumed zero).

$$\beta = \frac{D_\alpha}{D_\beta}$$

erf = error function

The concentrations at the various boundaries were taken from the Zr-O and Zr-N phase diagrams. The values for the diffusion coefficient of oxygen or nitrogen in beta-zirconium were assumed to be the same as those determined by Mallet et al (2) for diffusion in beta-zircaloy 2.

The diffusion coefficients of oxygen and nitrogen in alpha-zirconium were calculated by the simultaneous solutions of equations (I) and (II) and are listed in Table I and plotted in Fig. 2. The Arrhenius equation for the diffusion coefficient of oxygen in alpha-zirconium is:

$$D_{\alpha}, \text{ cm}^2/\text{sec} = .030 e^{-\frac{39,000 \pm 1000}{RT}}$$

This is in good agreement with the results of Remler (3) for iodide zirconium, and Mallett et al (2) for Zircaloy-2.

Limited data indicate that the diffusion of nitrogen is about 20 times slower than oxygen in alpha-zirconium. The equation for the diffusion coefficient of nitrogen in alpha-zirconium, based on data at 900° and 1100°F, is given by:

$$D_{\alpha}, \text{ cm}^2/\text{sec} = 1.9 e^{-\frac{57,000}{RT}}$$

Distribution of Gas During Scaling

In the scaling reaction the amount of gas dissolved in zirconium per sq. cm. of initial surface area, S, was determined by utilizing the following solutions to the diffusion equation:

$$\text{Below } 862^{\circ}\text{C: } S = 2C_S \sqrt{\frac{D_{\alpha} t}{\pi}}$$

$$\text{Above } 862^{\circ}\text{C: } S = 2(C_S - C_{II,I}) \sqrt{\frac{D_{\alpha} t}{\pi}} + C_{II,I} X_{\alpha} + 2C_{I,II} \sqrt{\frac{D_{\beta} t}{\pi}}$$

Here, the concentrations (gm/cm³) are the same as defined before and X_α is the thickness (cm) of the alpha-diffusion zone. Values of D_α below 862°C were extrapolated from the Arrhenius plot, Fig. 2.

The amount of gas dissolved in zirconium as a function of time at temperature is shown in Fig. 3 for air-runs neglecting nitrogen pickup. After breakaway, the amount of gas dissolved in the metal is represented as being the same as that existing immediately before breakaway since the depth of the diffusion zone remains relatively constant. The amount of

dissolved gas subtracted from the total weight-gain gives the amount of gas contributing to scale formation.

In air-runs, the amount of gas dissolved before breakaway (primarily oxygen) ranges from 25 to 50%, depending on temperature. The maximum occurs at about 900°C. In oxygen-runs, the percentage of gas dissolved would be somewhat higher since the scaling rate in air is greater than that in oxygen.

In nitrogen-runs, about 95% of the total weight-gain is due to nitrogen dissolution; only 5% contributes to scale formation.

From the amount of gas contributing to scale formation, the equivalent depth of metal consumed in air-runs may be calculated. But, in air studies in the range from 700-1050°C, another factor must be considered. In this temperature range growth occurs by a deformation process, i.e., the surface area is increased with a corresponding reduction in thickness. Thus, during scaling the metal is reduced in thickness by scale formation and by deformation. The total depth of metal "consumed" is shown in Fig. 4 as a function of time at temperature for various grades of zirconium and Zircaloy-2.* The initial specimen thickness was 1/16". The breakaway times and average growth rates which were utilized in computing the depth of metal "consumed" by deformation in air-runs are assembled in Table II, along with similar data for oxygen-runs.

*To obtain reduction in metal thickness, multiply by 2.

In general, breakaway occurs at shorter scaling times and the growth rate increases as: a) the impurity level of zirconium is raised, and b) the scaling atmosphere is changed from oxygen to air.

Lastly, it should be noted that Fig. 4 represents the findings with 1/16" plate specimens. Metal consumption with either thinner or thicker specimens would probably be less since the growth rate appears to be at a maximum with 1/16" thick specimens.

Future Work

Experimental work will continue in order to determine the exact mechanisms by which zirconium grows in air and oxygen. As a portion of this work, the possibility of the outward diffusion of zirconium above 1000°C will be investigated further.

References

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TABLE I : DIFFUSION OF OXYGEN AND NITROGEN IN ALPHA-ZIRCONIUM

| <u>TEMP., °C</u> | <u>MEDIUM</u> | <u>RATE OF MOVEMENT (k) OF ALPHA DIFFUSION ZONE*, cm²/sec.</u> | <u>DIFFUSION COEFFICIENT cm²/sec.</u> |
|------------------|---------------------------|---|--|
| 900 | AIR OR OXYGEN NITROGEN | 1.1 X 10 ⁻⁸ 2.7 X 10 ⁻¹⁰ | 2.2 X 10 ⁻⁹ 4.5 X 10 ⁻¹¹ |
| 1000 | AIR OR OXYGEN | 3.3 X 10 ⁻⁸ | 1.2 X 10 ⁻⁸ |
| 1100 | AIR OR OXYGEN NITROGEN | 6.4 X 10 ⁻⁸ 4.0 X 10 ⁻⁹ | 2.9 X 10 ⁻⁸ 1.6 X 10 ⁻⁹ |
| 1200 | AIR OR OXYGEN | 1.6 X 10 ⁻⁷ | 8.4 X 10 ⁻⁸ |

* $k = \frac{x^2}{t}$, WHERE x IS THE DEPTH OF THE ALPHA-DIFFUSION ZONE,
AND t IS THE SCALING TIME IN SECONDS.

TABLE II: BREAKAWAY TIMES AND GROWTH RATES OF VARIOUS GRADES OF ZIRCONIUM IN AIR AND OXYGEN.

| <u>TEMP., °C</u> | <u>IODIDE</u> | | <u>ARC-MELTED SPONGE</u> | | <u>GRAPHITE MELTED</u> | | <u>ZIRCALOY-2</u> | |
|--|----------------------|------------|--------------------------|-----------------------|------------------------|---------------------|--------------------------------|-----------------|
| | <u>O₂</u> | <u>AIR</u> | <u>O₂</u> | <u>AIR</u> | <u>O₂</u> | <u>AIR</u> | <u>O₂</u> | <u>AIR</u> |
| <u>BREAKAWAY TIME → HOURS</u> | | | | | | | | |
| 600 | » 100 | » 300 | — | 300,82 ^a | — | 30,20 ^d | 8 ^b ,3 ^c | 9 ^d |
| 700 | » 100 | 270 | 100 | 45,95,15 ^a | 10 | 11,5 ^d | 3 ^b ,5 ^c | 3 ^{ee} |
| 800 | » 100 | 12 | 13 | 20 | 2 | 4,2 ^d | 3 ^b ,2 ^c | — |
| 900 | ~ 100 | .8 | 2.5 | 1 | .5 | .7,5 ^d | — | — |
| 1000 | — | 3 | .5 | .5 | 2 | 4,1 ^d | — | — |
| <u>GROWTH RATE (SURFACE AREA) ↔ %/HOUR</u> | | | | | | | | |
| 700 | — | .02 | 0 | .1 | 0 | .2 ^d ,2 | — | — |
| 800 | — | .5 | .04 | .3 | .02 | 4 ^d ,1.5 | — | — |
| 900 | .2 | 11 | .8 | 8 | 3 | 30 ^d ,9 | — | — |
| 1000 | — | 9 | .8 | 8 | 11 | 40 ^d | — | — |

a) KENDALL (5)

b) GULBRANSEN AND ANDREW (6)

c) MALLET AND ALBRECHT (7)

d) PHALNIKAR AND BALDWIN (8)

e) EXTRAPOLATED

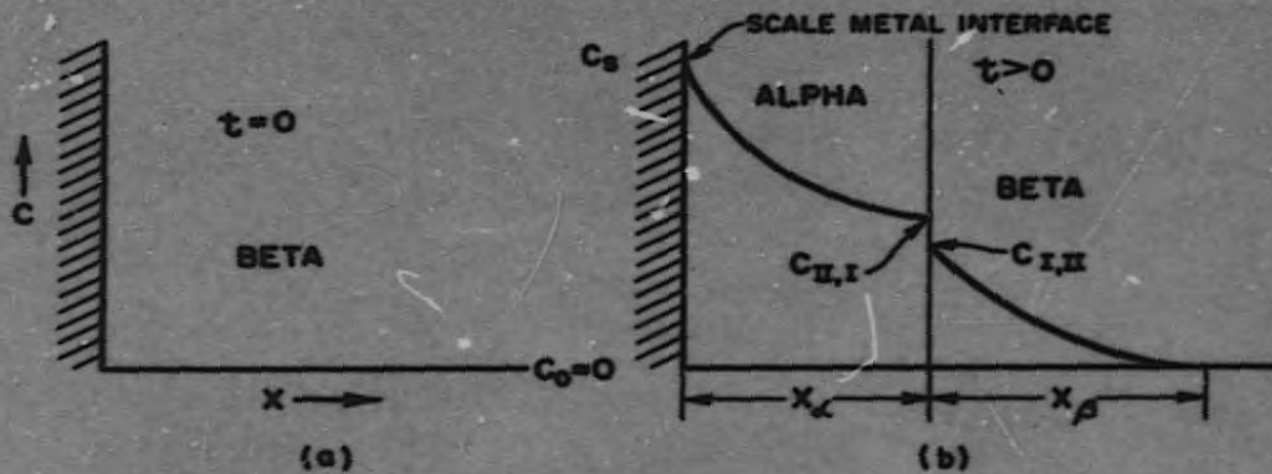


FIG. 1: DIFFUSION OF OXYGEN OR NITROGEN IN BETA-ZIRCONIUM ABOVE 862°C, THE ALPHA PHASE DEVELOPING FROM THE SCALE METAL INTERFACE. THE BETA PHASE TRANSFORMS TO ALPHA ON COOLING.

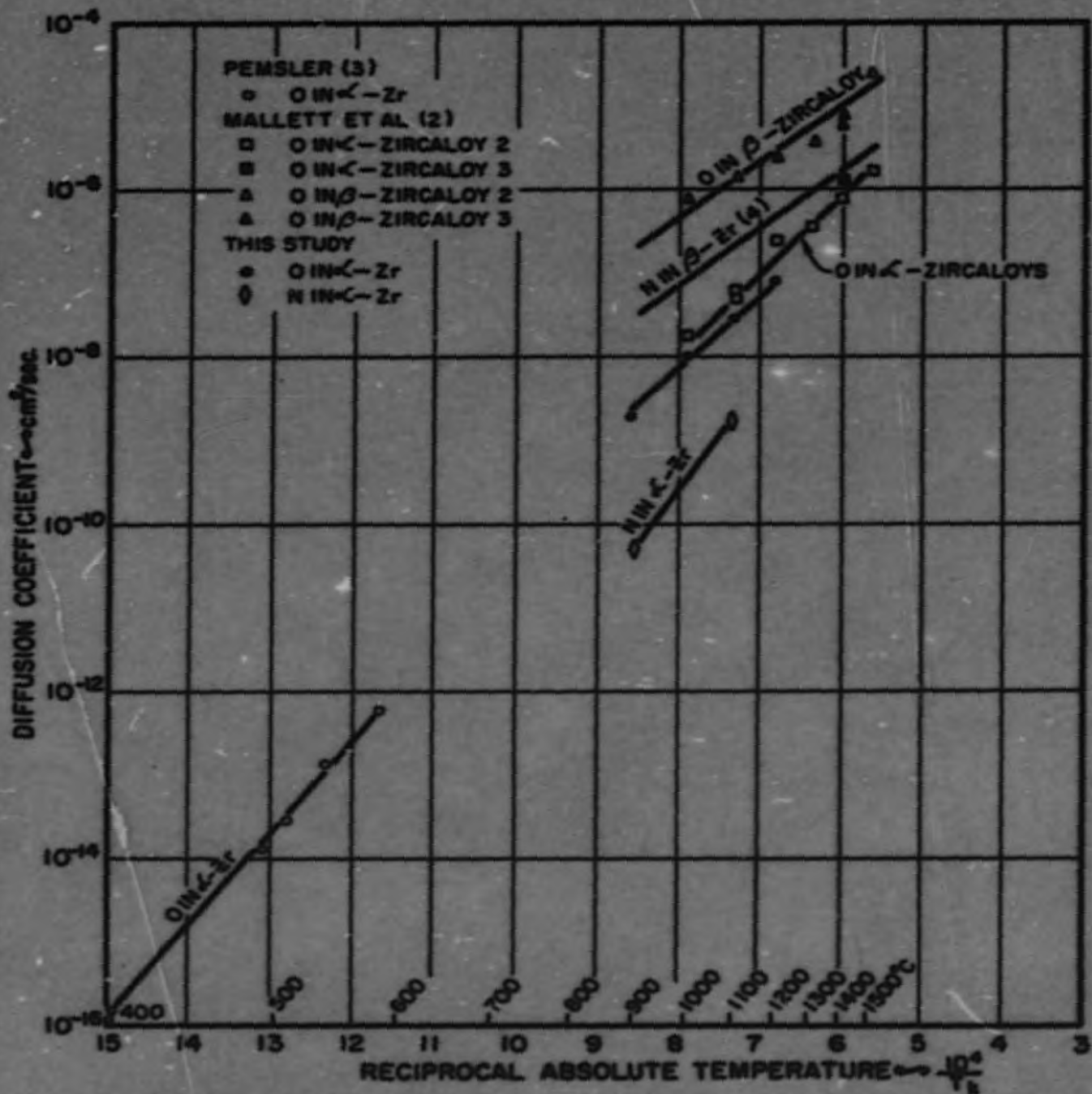


FIG. 2: DIFFUSION COEFFICIENT OF OXYGEN AND NITROGEN IN ZIRCONIUM AND ZIRCALOYS.

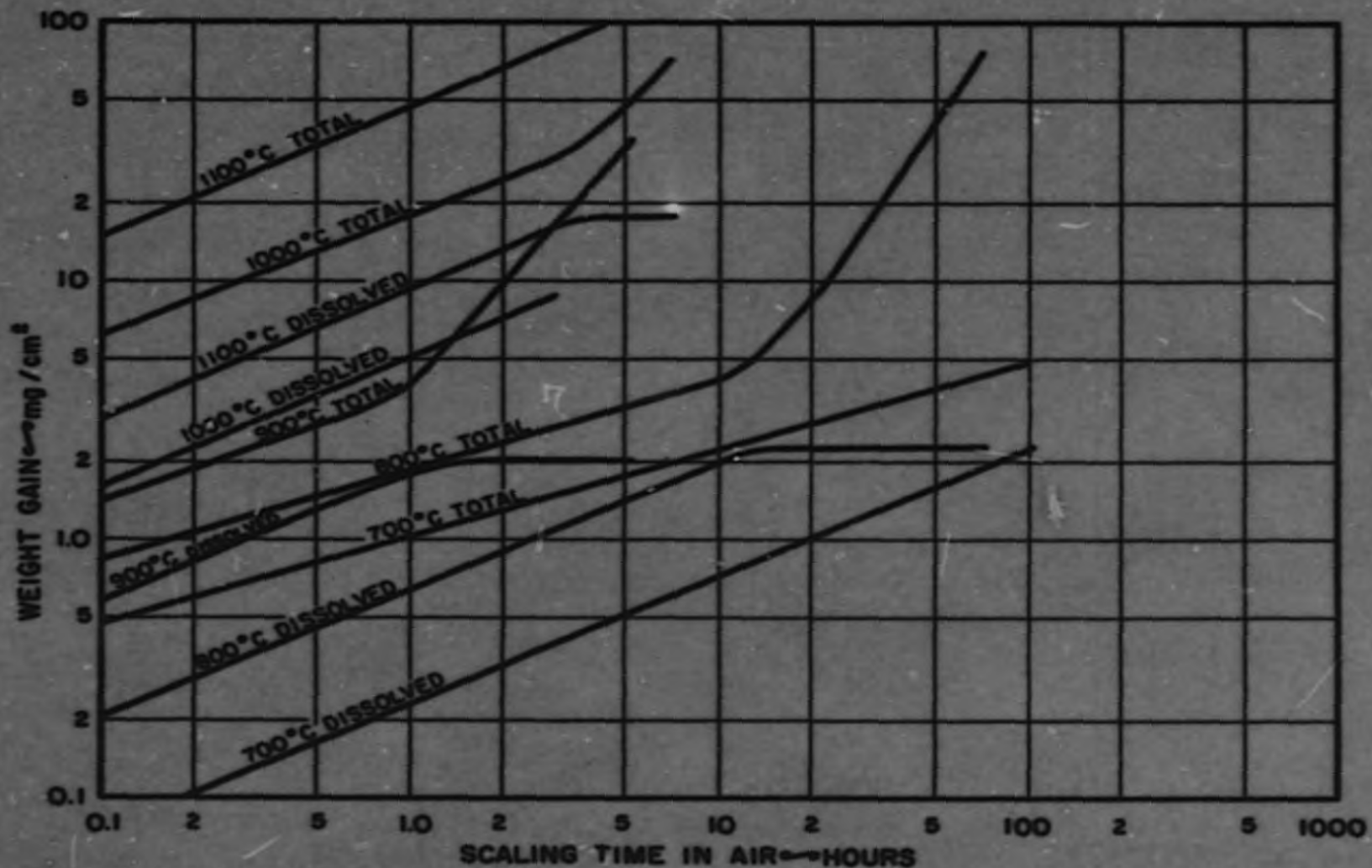


FIG. 3: TOTAL WEIGHT-GAIN AND WEIGHT OF GAS DISSOLVED IN THE METAL DURING SCALING OF IODIDE ZIRCONIUM IN AIR. TOTAL WEIGHT-GAIN MINUS WEIGHT DISSOLVED IN THE METAL EQUALS THE WEIGHT OF GAS CONTRIBUTING TO SCALE FORMATION.

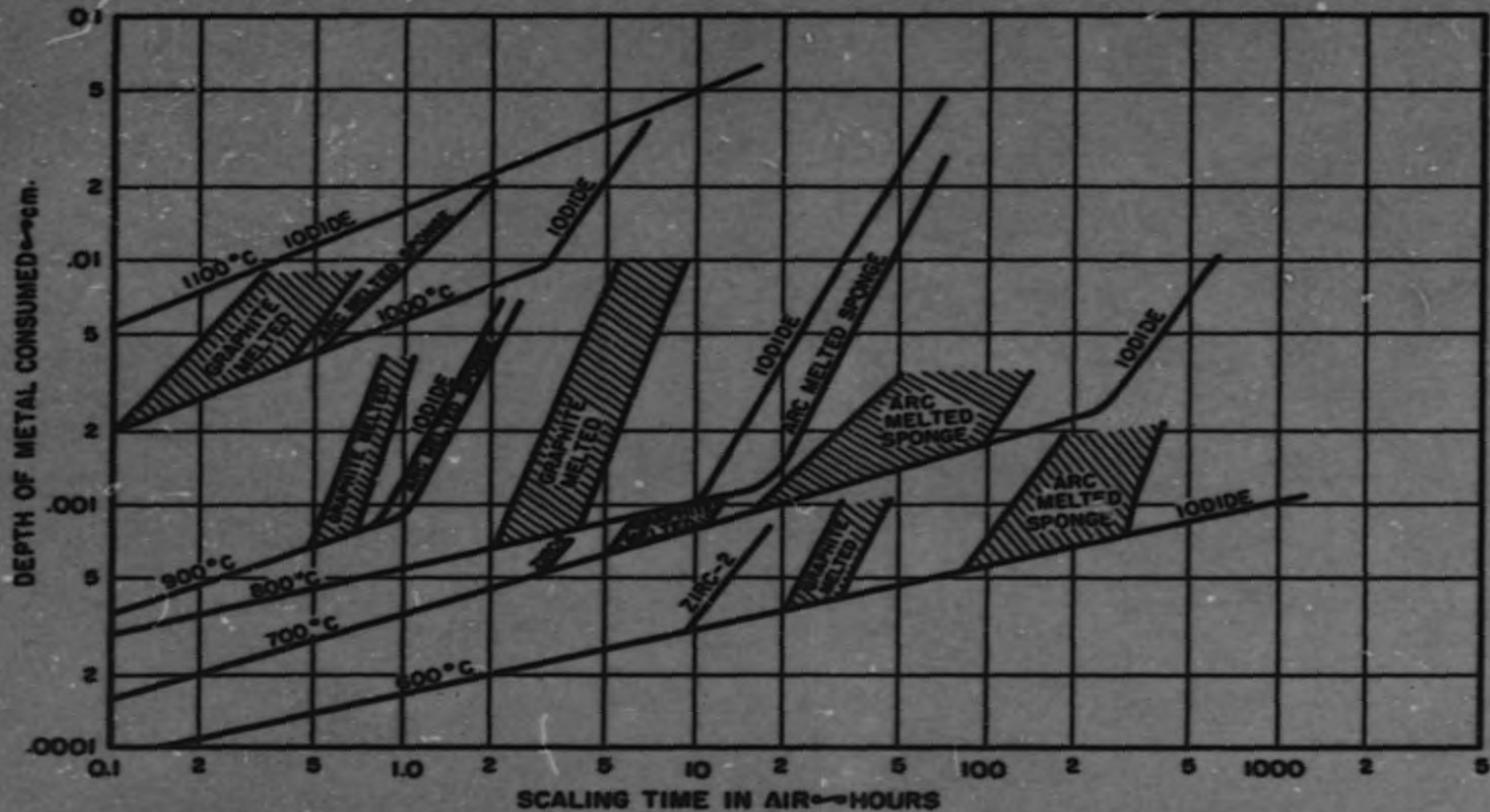


FIG. 4: DEPTH OF METAL CONSUMED IN THE AIR-SCALING OF VARIOUS GRADES OF ZIRCONIUM AND ZIRCALOY 2.

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