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CORROSION BEHAVIOR OF URANIUM-ZIRCONIUM ALLOYS IN HIGH TEMPERATURE WATER AND STEAM

by

S. Kass
K. M. Goldman

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ABSTRACT

The corrosion behavior of uranium-zirconium alloys containing 50 w/o U has been determined in high temperature water at 600 and 680°F and in steam at 750°F. Data for other compositions in the range of 10-60 w/o uranium are also presented to indicate the general effect of uranium content on corrosion behavior of uranium-zirconium alloys. It was found that, in general, the 50 w/o U-50 w/o Zr alloys are essentially unaffected by heat treatment. They exhibit a linear rate of corrosion at 680°F. These rates increase with increasing temperature according to the Arrhenius relationship. Corrosion life as a function of uranium content and temperature is presented and a mechanism of corrosion is suggested. The increase in total hydrogen content of the 50 w/o U - 50 w/o Zr alloys resulting from corrosion at 680°F in water is presented. From a comparison of oxidation data obtained in water with those obtained in dry oxygen at similar temperatures, it is concluded that hydrogen is probably not involved in the mechanism of corrosion of these materials because of the good agreement between the two kinds of data. This idea is further substantiated by data from another laboratory which indicates that the hydride formed in the 50 w/o U - 50 w/o Zr alloy is similar to $ZrH_{(1.2-1.4)}$ rather than to uranium hydride.

Corrosion Behavior of Uranium-Zirconium Alloys in High Temperature Water and Steam

S. Kass and K. M. Goldman

I. INTRODUCTION

The corrosion behavior of uranium-zirconium alloys in hot, pressurized water is a subject which has not received much, if any attention in the literature up to now, chiefly because of its classified nature. These alloys represent potential fuel materials for nuclear reactors and their corrosion behavior in hot pressurized water is of great interest to those interested in water cooled reactors.

The work described in this report is concerned principally with the corrosion behavior of an alloy containing 50% uranium and 50% zirconium by weight.

In order to understand more clearly the nature of the corrosion behavior of the alloy, compositions ranging from 10 to 60% uranium in zirconium were also studied. These studies have yielded information on the effect of uranium content not only on corrosion behavior as such but also on the response of the several alloys to heat treatment and the subsequent effect of heat treatment on corrosion resistance.

It will be shown that in hot water the corrosion is characterized by a linear rate for isothermal conditions. Furthermore, the role of hydrogen in the corrosion reaction will be discussed in terms of the rate of hydrogen build-up in the alloy and the general behavior of hydrogen in the Zr-50 w/o U alloy.

In addition, the behavior of the Zr-50% U material in hot water will be compared to its behavior in dry oxygen.

I. HOT WATER CORROSION

Experimental Procedure

The ingots were prepared from sponge zirconium and derby uranium by double-arc melting (vacuum). They were subsequently forged and hot rolled to 0.150 in. strip. Suitable heat treatments were performed in sealed vycor bulbs previously evacuated to less than 0.03 microns to which helium at 25 cm Hg pressure was added.

Corrosion test specimens 1 in. x 0.5 in. x 0.1 in. were machined to a 63 rms finish from the heat treated 0.150 in. thick strip. Before testing in 600° and 680°F water and 750°F steam at 1500 psi using techniques which have been previously reported[1], the specimens were washed in Alconox, rinsed 30 minutes in tap water, rinsed in ethyl alcohol and dried.

After each test period, the specimens were scrubbed with a soft brush to remove all loose oxide and weighings were made to the nearest 0.2 milligrams.

Experimental Results

Introduction

The corrosion behavior is represented in terms of weight change during corrosion testing as function of time in test for a given test temperature. Several heat treatments were represented for the several different compositions. Rate constants were calculated from the graphically determined slopes. These rate constants have been plotted as a function of uranium content for a given temperature. The effect of temperature on rate constants has been determined by plotting the logarithm of the rate constant as a function of the reciprocal of the absolute test temperature as well as rate constants versus temperature on linear coordinates. The influence of hydrogen on the corrosion behavior of these

alloys is indicated in curves showing hydrogen pickup as a function of corrosion weight loss and time.

General Behavior

The 680°F water corrosion behavior of 50% U-Zr alloy is shown in Figure 1 in which the weight change is plotted as a function of time for various heat treatments studied. It is noted for these alloys the weight change is generally a weight loss and the experimental points can be fitted by a single straight line. Thus an equation of the form $W = Kt$ can be written to represent the relation between weight loss and time. It is reasonably evident that the effect of heat treatment on corrosion behavior is insignificant in the U-50 w/o Zr alloy over the range of temperatures studied.

The Effect of Uranium Content on Corrosion Behavior

Curves similar to Figure 1 have been obtained for the alloys containing 10 to 60 w/o uranium and the rate constant for each alloy at each test temperature has been calculated. The family of curves shown in Figure 2 is obtained when the rate constants are plotted as a function of uranium concentration. This presentation of the data shows that at each given temperature the rate constant initially increases linearly with uranium content and then deviates sharply from linearity.

In 750°F steam at 1500 psi, the rate constant increases at about 35 w/o uranium. In 680°F water at 2708 psi and 600°F water at 1500 psi, the rate constant increases sharply beyond 50% uranium.

When the slopes of the linear portions of these curves are plotted as functions of temperature, a straight line relationship results (Figure 3). This relationship applies only to those specific composition ranges over which

the rate constant varies linearly with composition. Thus rate constants can be predicted over limited composition ranges for temperatures below 600°F and above 750°F.

Another interesting feature of the curves relating rate constants and uranium content is the position of their calculated intercepts. These are - 0.04 for 750, - 0.01 for 680, and - 0.005 for 600°F. They all indicate that the intercept on the corrosion rate coordinate (y axis) at zero uranium content (X = 0) is negative. This means that with no uranium in zirconium, corrosion rates are represented by weight gains rather than weight losses. This is an experimental fact[2].

The Effect of Composition and Temperature on Corrosion Life

It has been reported that certain uranium-base alloys initially show excellent corrosion resistance characterized by low corrosion rates followed by a short period of accelerated corrosion and disintegration (discontinuous failure), resulting from the formation of uranium hydrides. Corrosion life has been defined as the total exposure time preceding the onset of cracking and disintegration. Uranium-zirconium alloys after appropriate heat treatments exhibit discontinuous failure. Generally, the mode of failure of the alloys described here is not that of severe cracking. The data presented in Figure 4 illustrate the corrosion lives of the alloys in 750°F steam and 600° and 680°F water as functions of uranium content. (The bars marked X signify failure.) This presentation indicates, (1) alloys containing 10, 15 and 20 w/o uranium exhibit very long lives at all temperatures, (2) the corrosion life at 680° and 750°F decreases with increasing uranium content, and (3) the corrosion life of the 35 and 50% alloys decreases markedly with temperature increase from 680°F to 750°F.

The fact that the alloy compositions described above, particularly the U-50 w/o Zr, do not generally fail by severe cracking suggests that the

mechanism of corrosion is not associated with hydrogen. This is substantiated later in this paper by two pieces of evidence; (1) behavior in oxygen is similar to that in water; and (2) a hydride of zirconium forms in this system rather than a hydride of uranium[4].

The Effect of Temperature on Corrosion Rate

The corrosion rate of the alloys containing 10 to 35 w/o uranium appears to be a linear function of temperature over the range studied (Figure 5). On the other hand, the 50 and 60 w/o alloys differ markedly; the corrosion rates sharply increase with higher test temperatures.

The straight line relationship as predicted by the Arrhenius equation is obeyed by the 50 and 60 w/o alloys and not by the 10 to 35 w/o alloys when the logarithm of the corrosion rate is plotted against the reciprocal of absolute temperature (Figure 6).

Hydrogen Reactions During Corrosion

During exposure to hot water, uranium-zirconium alloys exhibit an increase in hydrogen content as a result of the corrosion reaction. The manner in which the hydrogen content increases with time is shown in Figure 7. Weight loss data are shown on the same figure for comparison. It is seen that, in general, hydrogen content increases with time in much the same way as weight loss. Data are shown for material in the epsilon as well as in the gamma-condition. If hydrogen content is plotted against weight loss, the relationship shown in Figure 8 results. The relationship between hydrogen content and weight loss appears to be the same for epsilon and gamma-material. These curves show only the total hydrogen content. What is possibly of more interest is the hydrogen pickup in terms of the percent of theoretical hydrogen. That is; (observed-intial)/theoretical x 100. A plot of percent of theoretical hydrogen vs time is shown in Figure 9. Again for both gamma and epsilon material

corresponding to the data of Figure 8, the following observations should be made:

1) For the material initially in the epsilon phase, there is an incubation period of 8 to 10 days during which little or no hydrogen pickup is observed.

2) For the gamma-quenched material, an incubation period of approximately 20 days exists before significant hydrogen pick-up is observed.

3) Once the incubation periods are exceeded, the percent of theoretical hydrogen increases at a rate which decreases with time. The rates appear to be the same for both materials.

4) The hydrogen pickup in epsilon material appears to be approaching a level somewhere under 3% of theoretical whereas that of the gamma-material is somewhere under 2%.

5) All samples contained a hydride phase because the hydrogen content of the starting material exceeded the terminal solubility of hydrogen in U-50 w/o Zr alloy (approximately 40 ppm at 360°C)[4].

III. OXIDATION IN OXYGEN

A. General

The oxidation of Zr-50 w/o U in oxygen has been studied both at Bettis and at Westinghouse Research Laboratories. The work at Bettis consisted of oxidizing samples in the epsilon condition in pure oxygen at 350, 400, 546, 620, 750, and 800°C for times varying from one hour to 52 days. Oxidation rates

were obtained by metallographically measuring the unreacted metal. The structure of the oxide scale was studied by X-ray analysis and metallography.

The work at the Westinghouse Research Laboratories[3] supplemented the data obtained at Bettis and provided data on the oxidation of Zr-50 w/o U in oxygen at 200-500°C. In these experiments, starting material was both in the epsilon and in the gamma conditions. Oxidation rates were measured by weighing the samples after they had been oxidized in oxygen for various lengths of time at the above-mentioned temperatures. Oxidation layers were analyzed chemically for U and Zr and observed metallographically. X-ray patterns were also taken.

B. Discussion of Oxygen Data

The data obtained by both laboratories, Figure 10, show some discrepancies. Activation energy values calculated from the slopes of these lines are as follows: 16,300 cal/mole for the data from Bettis (epsilon), and 24,000 (epsilon) and 21,000 cal/mole (gamma) for the data from Westinghouse Research. Furthermore, the water data appear to fall only on the curve of the Bettis oxidation data. It should be noted that the Bettis data for both water and oxygen were obtained on material from the same ingot. The data reported by Westinghouse Research Laboratories were obtained on material made at a different time. Slight differences on impurities or heat treatment may be responsible for the difference in behavior. The fact that the water and oxygen data appear to follow a similar curve indicates that, very probably, the mechanism of corrosion in hot water is not influenced by hydrogen which is produced as a result of the corrosion reaction. Although these alloys do, in fact, increase in hydrogen content during corrosion testing in water, the hydride that is formed in the U-50 w/o Zr alloy is similar to $ZrH_{(1.2-1.4)}$[4]. The fact that a zirconium hydride

is formed rather than a uranium hydride, could provide an explanation for the lack of influence of hydrogen on the corrosion mechanism of this alloy.

C. Analysis of Oxide Structure

1. X-Ray Analysis

The phases present in samples oxidized in oxygen were determined as a function of distance from the gas/oxide interface for several temperatures and are given below:

Distance Below Oxide-Gas Interface (Inches)	Temp. °C	Phases Present
0	400	Tetragonal oxide
0.001		Tetragonal oxide
0.002		
0		UO_2
0.001	620	
0		UO_2, U_2O_5, U_3O_8
0.001	700	UO_2, Zr, U
0.002		
0		UO_2, U_3O_8, U_2O_5, ZrO_2
0.001	900	UO_2, U_2O_5, U_3O_8, Zr
0.002		

Several pertinent observations should be noted:

a. At 700°C, alpha zirconium and alpha uranium were both present in the metal adjacent to the metal/oxide interface. Below 700°C there was no evidence pointing to their existence.

b. Above 800°C, two layers separated the oxide and the base metal. The layer next to the oxide is alpha zirconium rich in oxygen. The second layer (next to the base metal) is presumed to be epsilon because it

has the same hardness as the base metal. Immediately adjacent to this second layer particles of alpha zirconium appear and are larger than in the base metal.

c. At 750°C, alpha zirconium, rich in oxygen, first appears between the oxide and metal.

d. At 546°C, only oxide and epsilon are present.

e. At temperatures below 620°C, a tetragonal oxide of c/a = 0.95 is formed whereas above this temperature, UO_2 and the higher oxides of uranium are formed.

An X-ray pattern of the corrosion product formed on a specimen tested in water at 360°C indicated that this corrosion product is very similar to that formed in oxygen at the same temperature. There appears, however, several extra lines in the pattern of the water formed oxide, probably caused by a hydration phenomenon.

Composition of Oxides

The chemical composition of the surface oxides produced during oxidation runs at temperatures varying from 300 to 500°C and on materials of two different initial structures epsilon and gamma was practially independent of these variables[3]. Analyses were in the range of:

U - 40.8 ± 0.8 w/o

Zr - 37.6 ± 0.4

O - 21.6 (difference)

The U-Zr weight ratio in the oxide, 1.08 was greater than that in the alloy 0.99, indicating some preferential migration of uranium into the oxide layer.

Density of the oxides formed was found to be 7.6 gm/cm^3 at 30°C. That of the alloy is 9.8. The ratio of the volume of oxide produced to the

volume of the metal reacted is 1.6. Since this is greater than 1, shrinkage of the oxide would not be expected according to Pilling and Bedworth. In other words, this oxide should offer some protection. On the other hand, the ratio is high enough to indicate that the oxide could be under compression so that cracking might be expected.

Thickness values calculated from the density and composition of the oxide were about 20% less than the thicknesses measured metallographically. This indicates a porous oxide.

The oxide actually does contain relatively large voids over the entire temperature range in both the epsilon and gamma alloys. The voids are elongated in the direction parallel to the oxide/metal interface which is a characteristic result of internal blistering in a film under lateral compression.

IV. DISCUSSION

This section is devoted to a discussion of several points of interest mentioned earlier in this paper. These will include general corrosion behavior of U-50 w/o Zr in hot water compared to that in oxygen, the effect of uranium on corrosion behavior, the effect of temperature on corrosion behavior, and hydrogen pickup during corrosion.

The comparison of the behavior of these materials in hot water and oxygen will be initiated by consideration of the factors characteristic of the behavior of these materials in these media.

These are summarized in the following tabulation:

Characteristic	Medium: Water	Medium: Oxygen
Oxidation Rate	Linear	Linear
Type of Weight Change	Negative (Non-adherent)	Positive
Hydrogen Pickup	Slight	None
Composition of Oxide Product		41%U-37%Zr-22%O
Activation Energy of Oxidation	16,000 cal/mole	16,000 and 24,000 cal/mole

The basic differences between the oxidation of U-50 w/o Zr in hot water and oxygen is that in water the oxidation product that is formed is non-adherent thereby effecting a loss of weight whereas in oxygen, the oxidation product is adherent and a gain in weight takes place. Furthermore, hydrogen is present in hot water oxidation whereas it is absent in oxygen oxidation.

Another look at Figure 10 is in order. It appears that the data obtained both in water and oxygen at Bettis are fitted reasonably well by a straight line whose slope yields an activation energy of approximately 16,000 cal/mole. The data from the Westinghouse Research Laboratories for the oxygen experiments yield a higher activation energy value, 21,000-24,000 cal/mole. All of these values are in the same order of magnitude indicating that hydrogen probably does not affect the rate of oxidation in hot water but may play a part in the nature of the oxide product formed. It should be re-emphasized that the role of hydrogen in hot water corrosion is minimized because a zirconium hydride rather than a uranium hydride is formed.

ACKNOWLEDGMENTS

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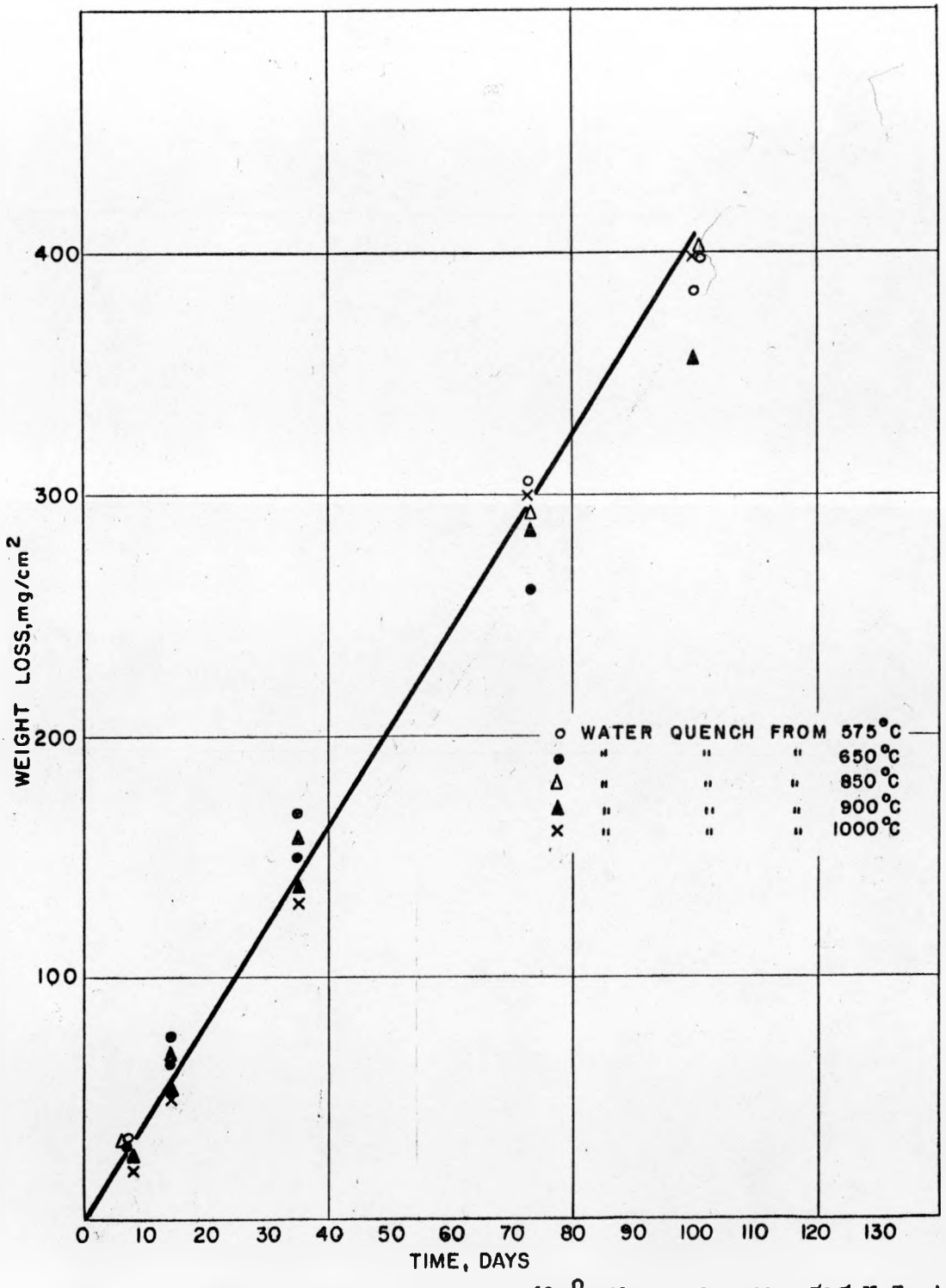

Fig. 1 - Weight Loss vs Time in 680°F Water for the 50% U-Zr Alloy In Several Heat Treatment Conditions

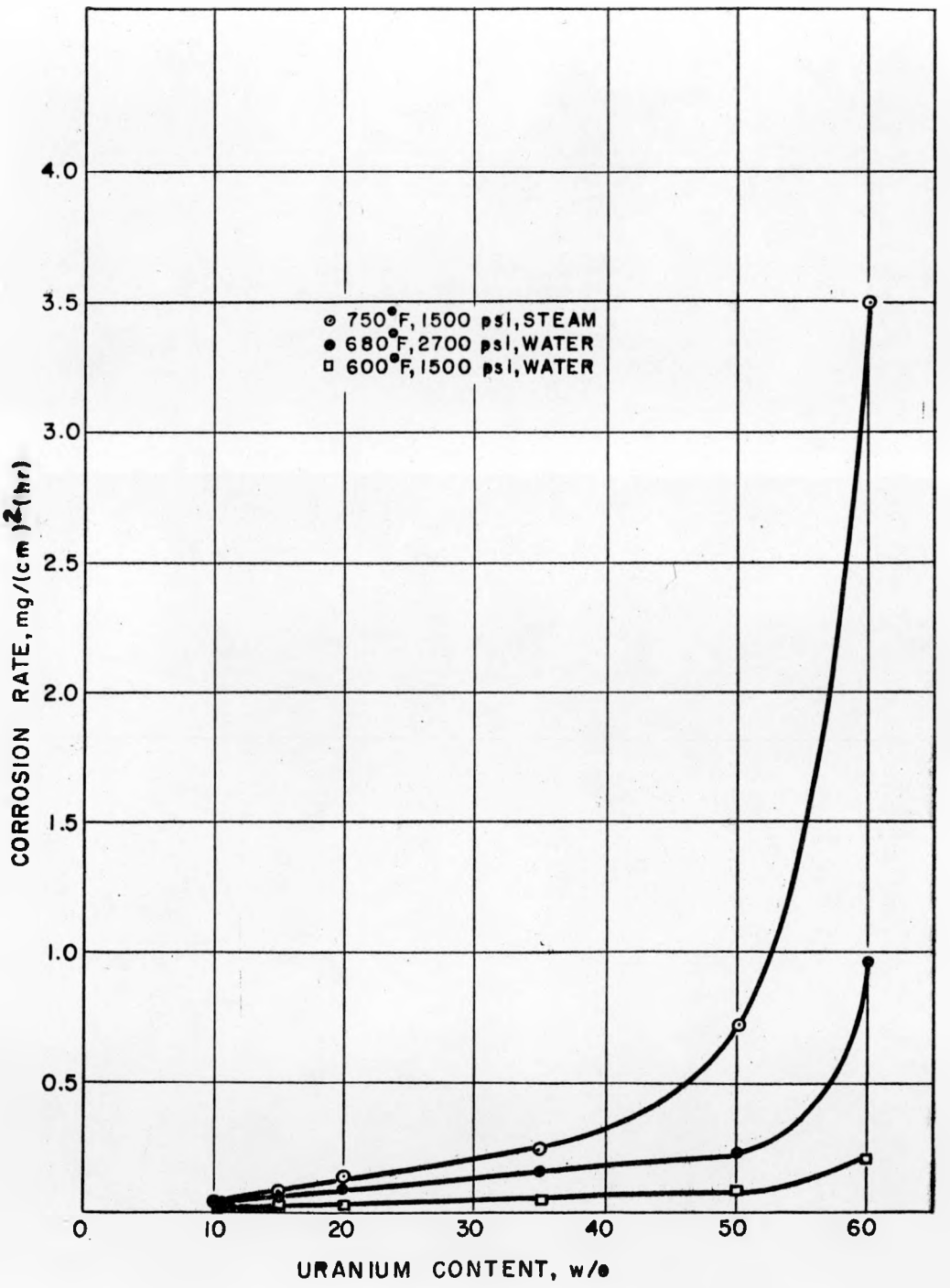

Fig. 2 - Corrosion Rate vs Uranium Content for Three Test Temperatures
Heat Treatment - Furnace Cooled from 575°C (Epsilon)

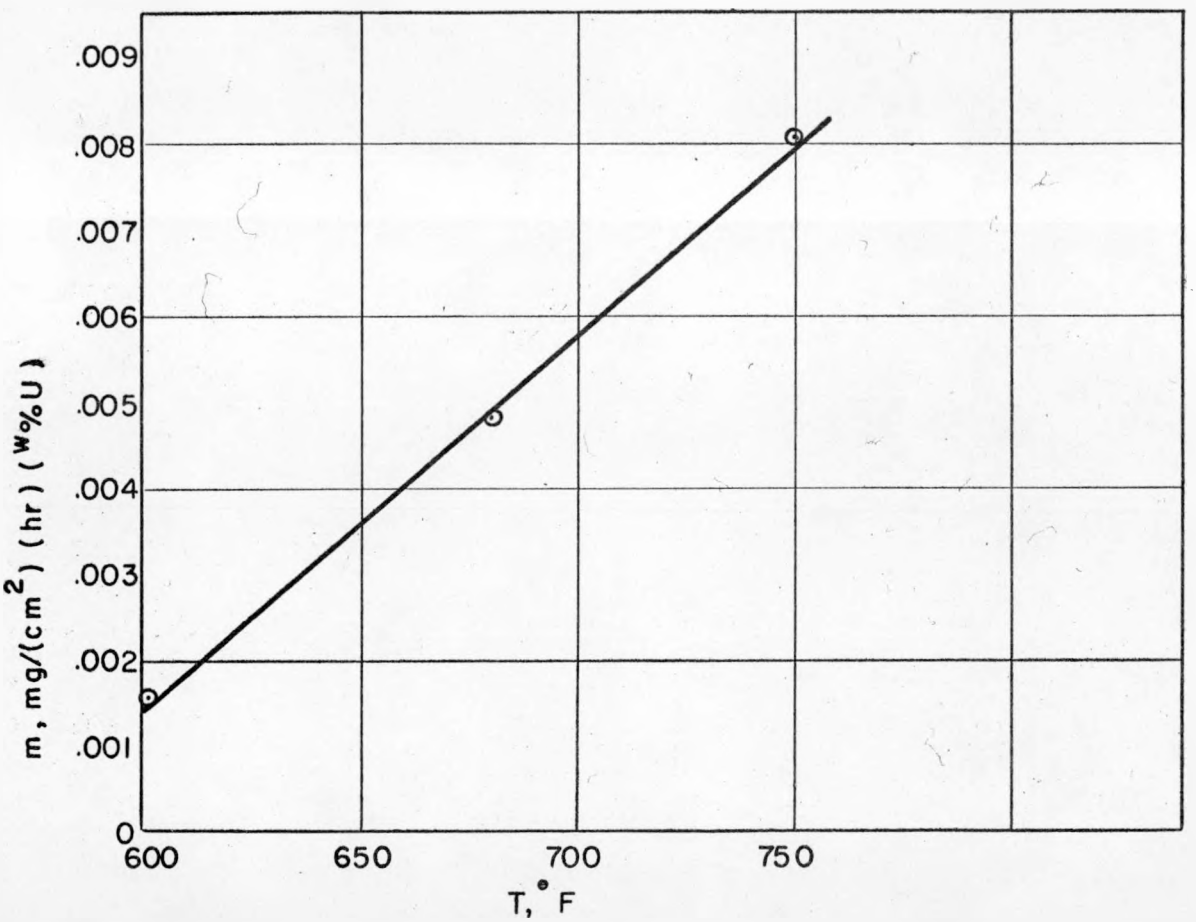

Fig. 3 - Slope of the Linear Portions of the Corrosion Rate vs Uranium Content Curves in Fig. 2 vs Temperature of Testing

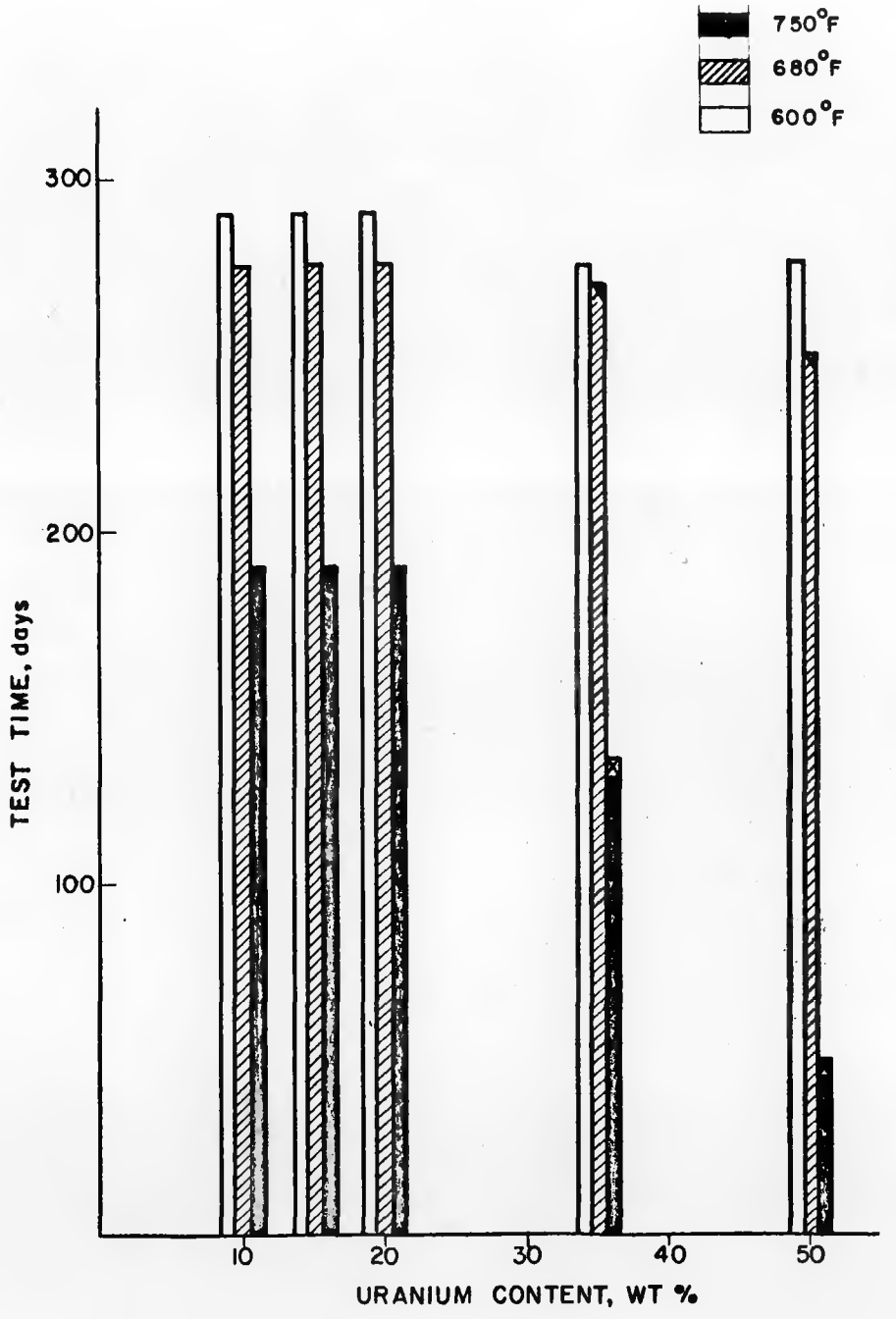

Fig. 4 - Corrosion Life vs Uranium Content at Three Test Temperatures
Heat Treatment - Furnace Cooled from 575°C (Epsilon)

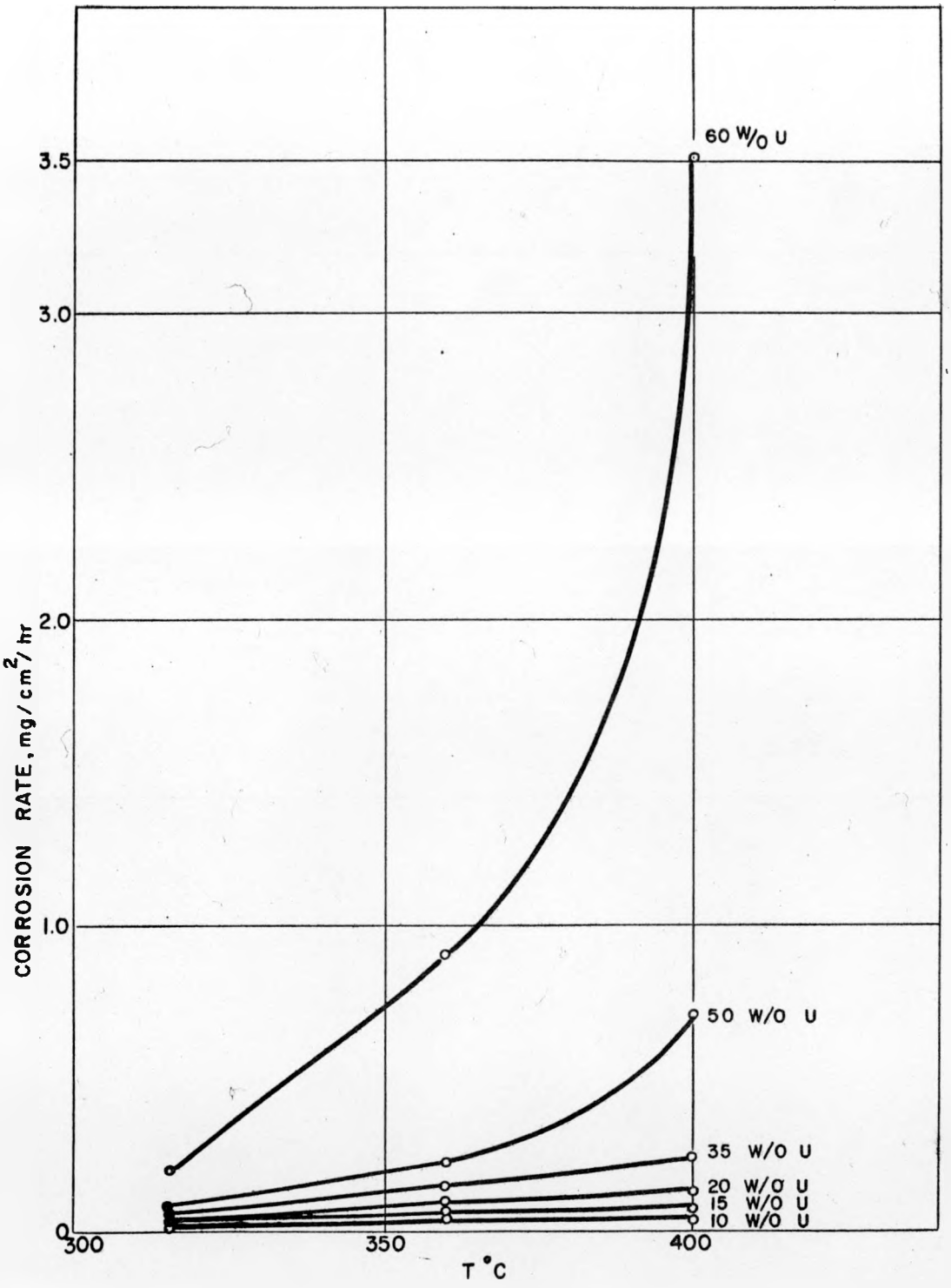

Fig. 5 - Corrosion Rate vs Temperature at 680°F Water for Several Alloy Compositions
Heat Treatment - Furnace Cooled from 575°C (Epsilon)

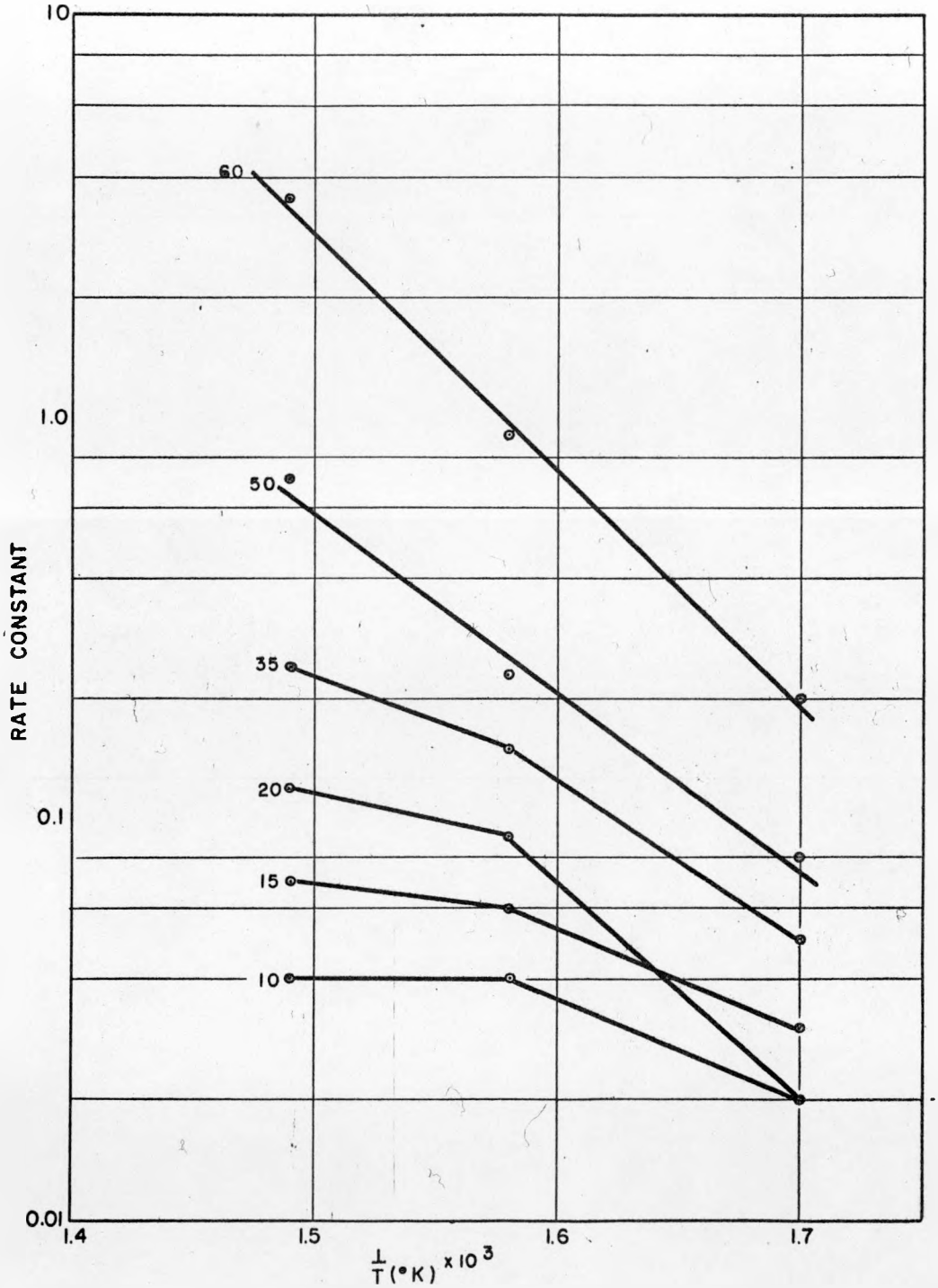

Fig. 6 - Logarithm of the Rate Constant vs Reciprical of the Absolute Temperature of Testing for Several Alloy Compositions

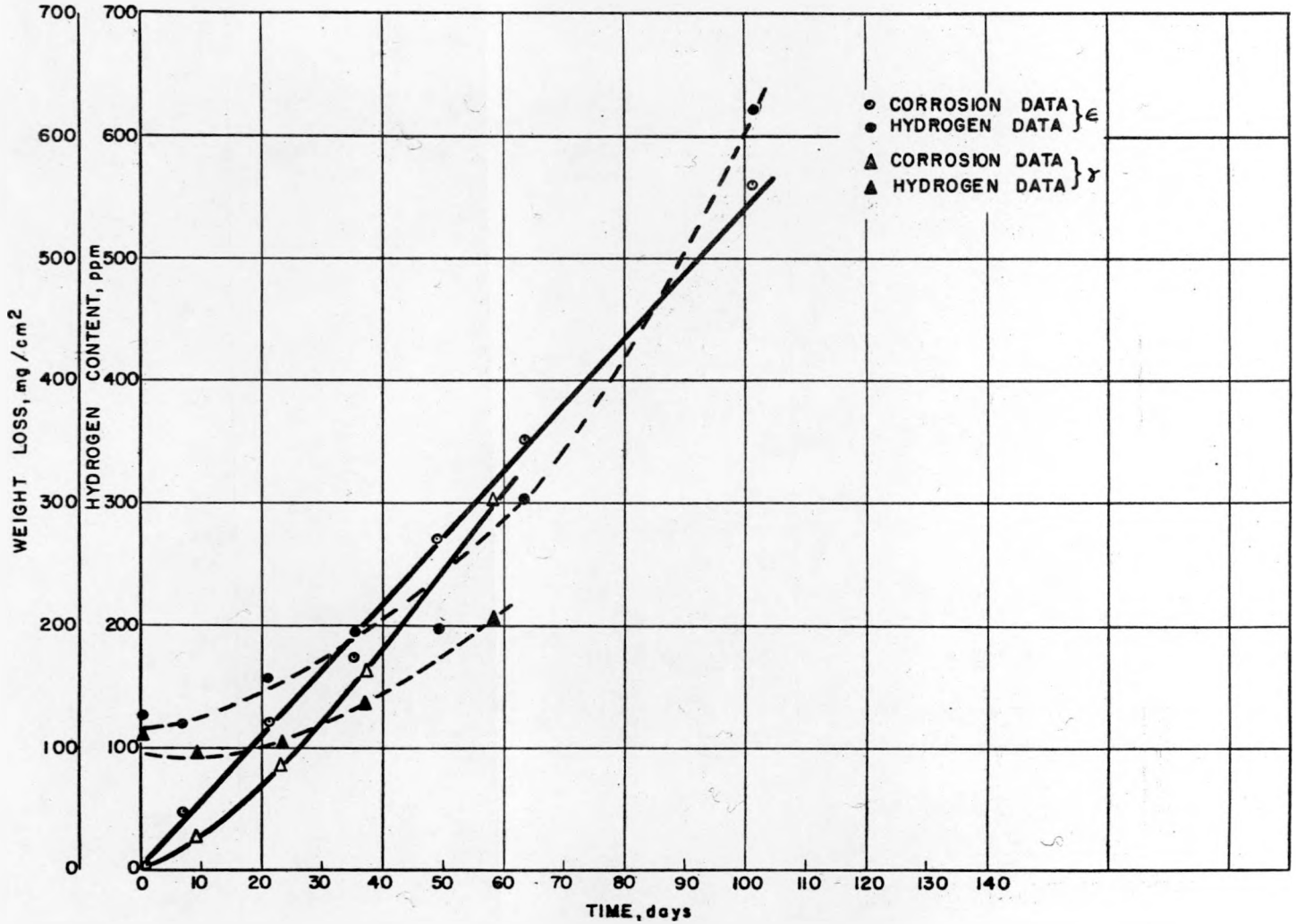

Fig. 7 - Weight Loss in 680°F Water and Hydrogen Content vs Time for the 50% U-Zr Alloy in Two Heat Treatment Conditions

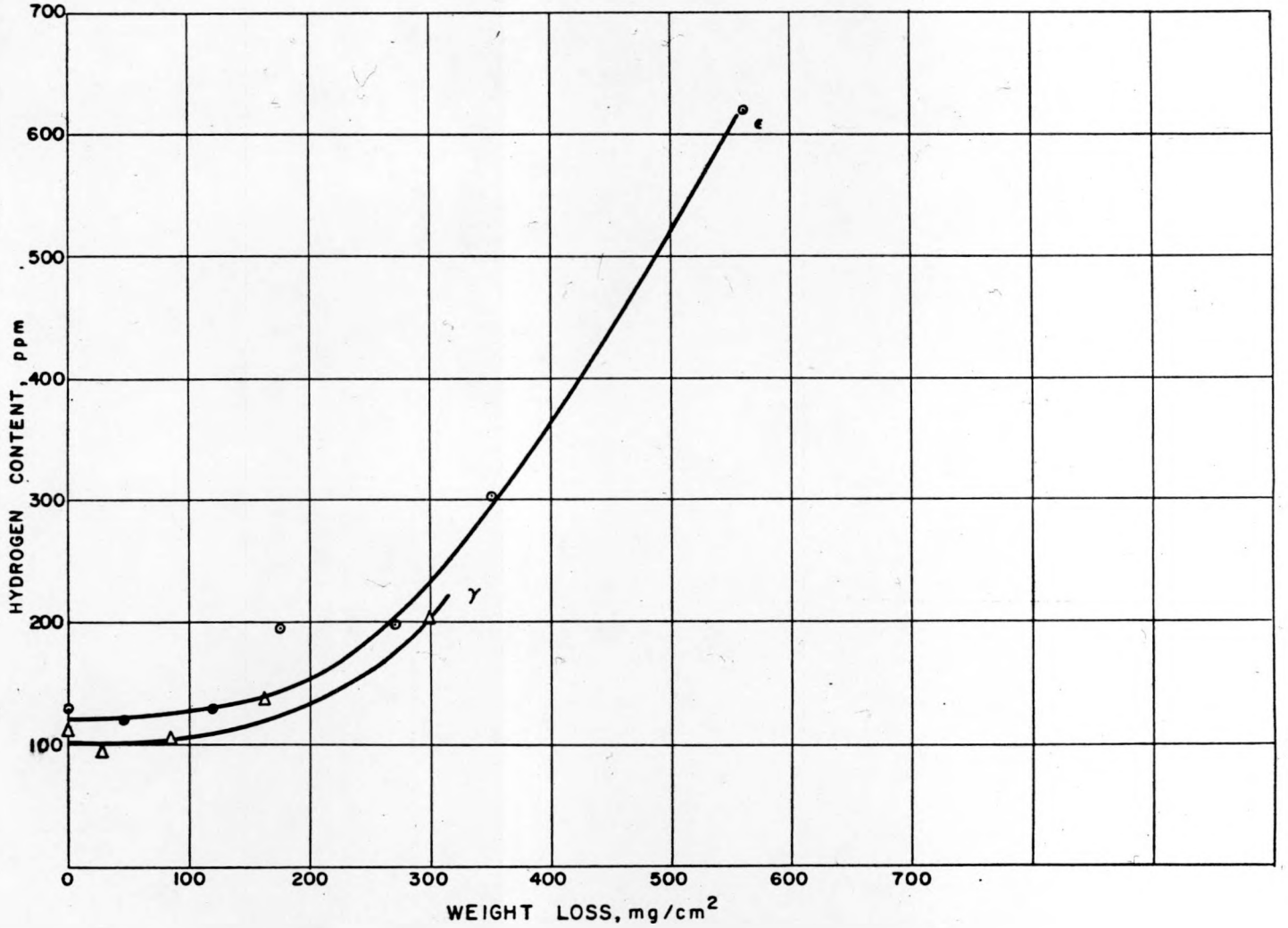

Fig. 8 - Hydrogen Content vs Weight Loss in 680°F Water for 50% U-Zr Alloy in Two Heat Treatment Conditions

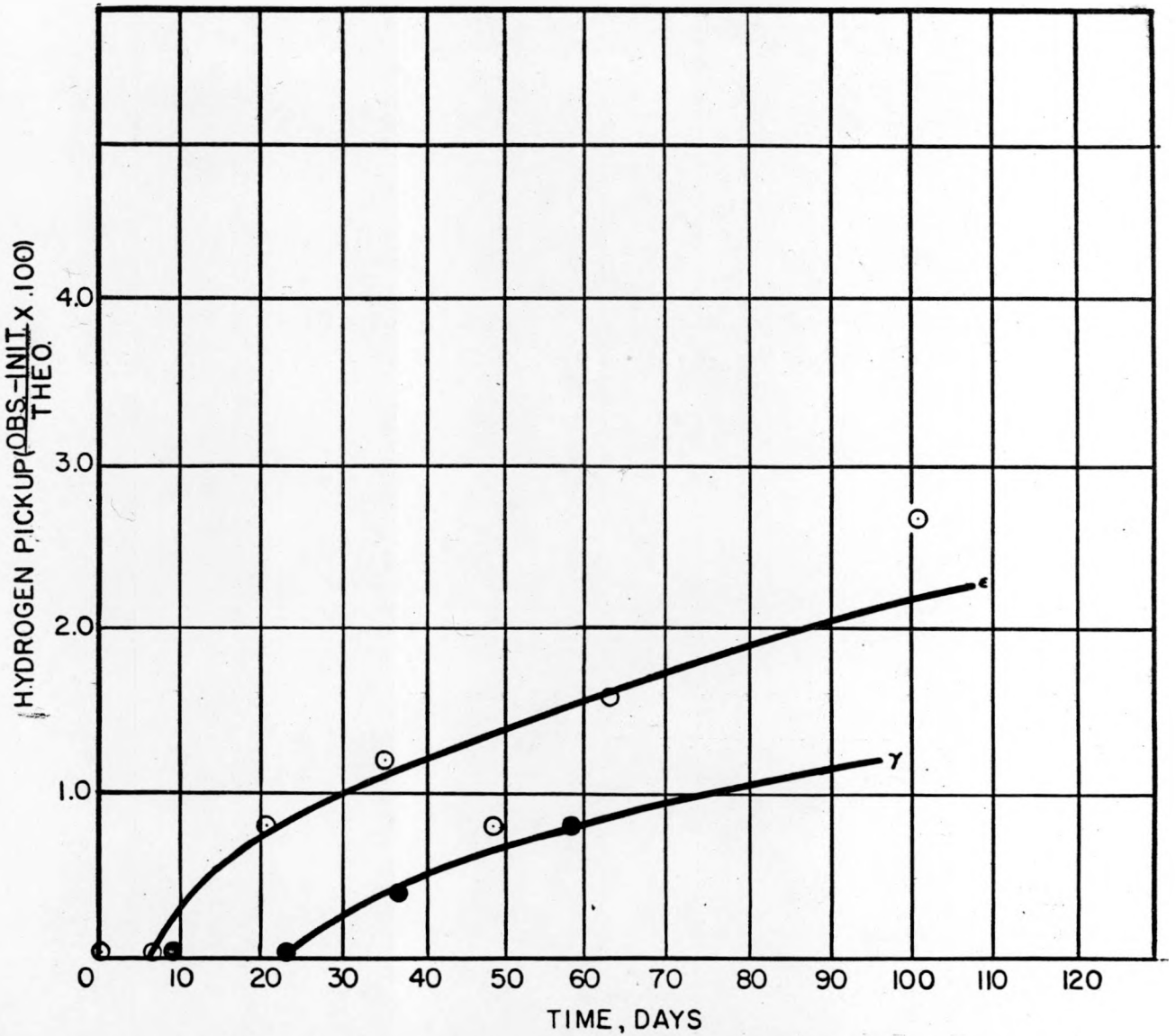

Fig. 9 - Percent of Theoretical Hydrogen Picked Up in 680°F Water Tests vs Time for 50% U-Zr Alloy in Two Heat Treatment Conditions

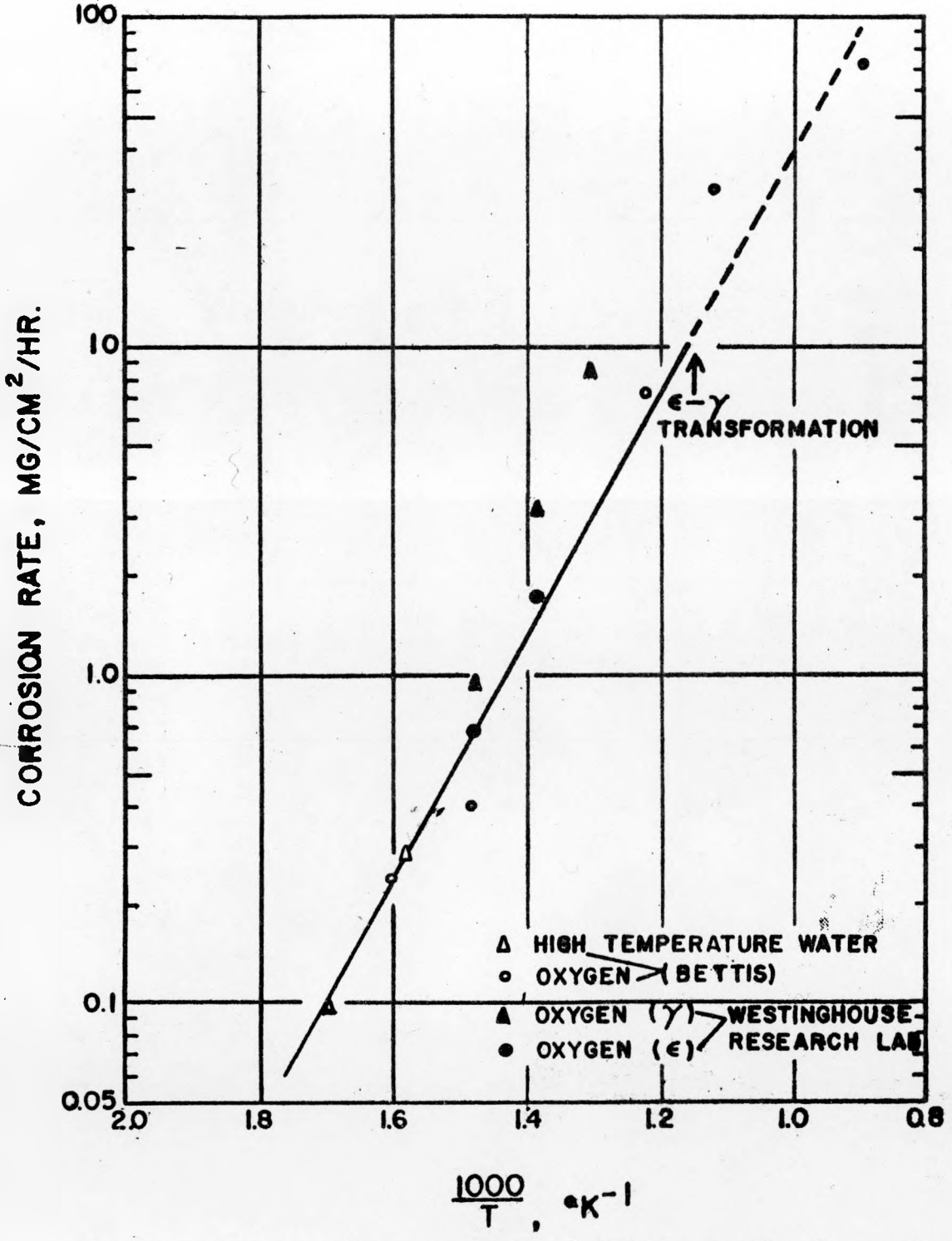

Fig. 10 - Corrosion Rates of Zr-50 w/o U Alloy in High Temperature Water and in Oxygen Gas