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THE ANNEALING OF IRRADIATION DAMAGE IN ZIRCALOY-2 AND THE EFFECT OF HIGH TEMPERATURE IRRADIATION ON THE TENSILE PROPERTIES OF ZIRCALOY-2

CRMet-922

by

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Chalk River, Ontario

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ABSTRACT

Tensile specimens of annealed and cold-worked Zircaloy-2 were irradiated at 380°C with 9.5×10^{19} n/cm^2 and tested at room temperature. In addition, annealed samples of Zircaloy-2, irradiated at 280°C with 7.7×10^{19} n/cm^2 and at 50°C with 9.1×10^{19} n/cm^2, were given isothermal and isochronal post-irradiation anneals and then tested at room temperature .

The annealed and cold-worked specimens irradiated at 380°C exhibited only a small amount of irradiation damage in contrast to specimens irradiated at or below 280°C which experienced considerable irradiation hardening. Results on the cold-worked material irradiated at 380°C indicated that the amount of normal thermal recovery of cold-work which occurred during the irradiation was virtually identical to that which occurred during an out-pile heat treatment at 380°C for the same length of time.

Analysis of the post-irradiation annealing data for the 50°C and 280°C irradiations revealed that in both cases the irradiation damage anneals out in the range 250°C to 400°C and is characterized by a single activation energy of approximately 2 eV throughout this range.

INTRODUCTION

In a previous study [1] the effect of neutron irradiation on the tensile properties of annealed and cold-worked Zircaloy-2, irradiated at 220°C with 3.6×10^{19} n/cm^2 and at 280°C with 2.7×10^{20} n/cm^2, was investigated. In this study it was found that:

1) a considerable increase in proportional limit, yield strength and ultimate tensile strength occurred in annealed and cold-worked Zircaloy-2 irradiated at 220°C and 280°C.

2) the normal thermal recovery of cold-work in Zircaloy-2 was not significantly altered by an irradiation at 280°C.

3) the post-irradiation annealing study indicated that the irradiation damage was annealing out very rapidly in the region of 350°C and was probably completely annealed out after 1 hour at 450°C.

4) there probably was a slight recovery of irradiation damage occurring in all the material during irradiation at 280°C (no recovery data was available for the 220°C irradiation).

5) a yield point appeared in irradiated annealed specimens tested at 280°C but not in irradiated specimens tested at room temperature.

The purpose of the present investigation was to:

1) study the effect of irradiating at a higher temperature than the temperatures used in the previous study.

2) investigate any possible enhanced thermal recovery of cold-work produced by irradiation at temperatures greater than 280°C.

3) study the post-irradiation annealing of irradiation damage in greater detail.

4) investigate further the yield point phenomenon found in the previous study in irradiated annealed Zircaloy-2 tested at 280°C.

In order to obtain answers to items (1) and (2), annealed and cold-worked Zircaloy-2 tensile specimens were irradiated at 380°C with 9.5×10^{19} n/cm^2. Annealed Zircaloy-2 tensile specimens irradiated at 50°C with 9.1×10^{19} n/cm^2 and at 280°C with 7.7×10^{19} n/cm^2 were used to study items (3) and (4).

EXPERIMENTAL DETAILS

(a) Material

The annealed, 13.1% cold-worked, and tempered 25.5% cold-worked Zircaloy-2 material used in this study was identical to that used previously, and a detailed account of the fabrication history as well as an analysis of the material used may be found in the report on the earlier work [1]. The 25.5% cold-worked material was tempered at 425°C for 15 minutes in order to produce specimens which had mechanical properties somewhat similar to 13.1% cold-worked material but which were in a different state of stability i.e. were structurally different.

(b) Tensile Tests

Tensile tests were performed using an Instron Tensile Machine which had been modified for use with active specimens. The tensile specimens were 0.160 inches in diameter and had a 1 inch gauge length. A crosshead speed of 0.05 inches/minute was used in pulling all the specimens. Post-irradiation annealing was carried out in a vacuum annealing furnace at a pressure of 1 μm of mercury. In order to obtain accurate values of the uniform % elongation, the load-elongation curves, as drawn by the Instron Tensile Machine, were corrected using the method outlined previously [1].

(c) Irradiation Details

One group of specimens was irradiated at 50°C with 9.1×10^{19} n/cm^2 in the NRX reactor in a uranium tube referred to as a low-temperature transformer rod. Two other groups of specimens were irradiated at 280°C with 7.7×10^{19} n/cm^2 and at 380°C with 9.5×10^{19} n/cm^2 in a high-temperature fast-neutron rod [2], a modified version of the low-temperature transformer rod. The neutron flux spectrum in both irradiation facilities is calculated to contain 50% fission neutrons and 50% with an E^{-1} distribution. In addition, the integrated fast-neutron flux values quoted in this report are calculated rather than measured and should be reliable to within 30%.

The maximum energy that a neutron of mass M_1 and initial energy E can give to a nucleus of mass M_2 is given by:

$$E_{max} = 4 M_1 M_2 E / (M_1 + M_2)^2$$

The energy E_d required to knock an atom out of its lattice site to form a separated interstitial and vacancy is about 25 eV. Substituting the value of 25 eV into the above equation, the minimum neutron energy (threshold) for the production of a displaced atom in zirconium may be calculated to be 582 eV. The flux values reported in this report pertain to neutrons with energies greater than 500 eV and thus all neutrons capable of displacing a Zr atom from its normal lattice position are included.

RESULTS

(a) Effect of Neutron Irradiation on Annealed and Cold-Worked Zircaloy-2 Irradiated at 380°C with 9.5×10^{19} n/cm^2.

The room-temperature tensile properties of annealed and cold-worked Zircaloy-2 irradiated at 380°C are given in Tables 1 and 2. Also shown for comparison are the results for irradiations at 50°C, 220°C and 280°C. Examining the results for the annealed material (Table 1), one sees that the effect of irradiation at 380°C is small compared to that at lower irradiation temperatures. Some irradiation damage does remain however after the 380°C irradiation as illustrated by the increase in proportional limit and yield stress and decrease in both the uniform and total elongations. The effect is much more pronounced in the case of the uniform elongation than the total elongation. From the scatter which exists in the ultimate tensile strength results it is difficult to ascertain whether the ultimate tensile strength was increased or not due to irradiation at 380°C. It appears most likely that the ultimate tensile strength was increased slightly since there was an increase in the ultimate tensile strength as well as the proportional limit and yield stress at the lower irradiation temperatures.

The results for the cold-worked material (Table 2) indicate that for both conditions of cold-working, the proportional limit, yield stress, and ultimate tensile strength have decreased during irradiation at 380°C when compared with unirradiated values whereas the same properties increased after irradiation at lower temperatures. If we now compare the irradiation results with those obtained on material held out-of-pile at the same temperature and for the same period of time we note the following:

1) recovery of mechanical properties occurred in both cold-worked materials during the out-of-pile anneal at 380°C for 41 days.

2) the small differences which exist between material irradiated at 380°C and material annealed out-of-pile at 380°C may be attributed to the presence of a small amount of irradiation damage in the irradiated material; this is consistent with the fact that a small amount of irradiation damage existed in annealed Zircaloy-2 after an irradiation at 380°C.

There appears to be no significant differences in the behaviour of 13.1% cold-worked material and tempered 25.5% cold-worked material during the irradiation at 380°C, a fact which also holds true for irradiations at lower temperatures.

(b) Post-Irradiation Annealing of Irradiation Damage

Samples of annealed Zircaloy-2 were irradiated at 50°C with 9.1×10^{19} n/cm^2 and at 280°C with 7.7×10^{19} n/cm^2 and then given various post-irradiation annealing treatments. Using the results of the previous study (1) as a guide, some of the irradiated specimens were given one-hour anneals at temperatures up to 400°C. These isochronal annealing results are tabulated in Tables 3 and 4 and are plotted in Figures 1 and 2. From the isochronal curves, it appeared that the recovery was most rapid in the region of 325°C and consequently some of the irradiated specimens were isothermally annealed at this temperature. Results are given in Tables 3 and 4 and are plotted in Figures 3 and 4.

Combining the isothermal and isochronal recovery data, using the method outlined in the Appendix, an activation energy was determined from the equation:

$$\ln \Delta\tau_i = c^1 - {}^{E}/KT_i \qquad \text{(Equation 8 - Appendix)}$$

where $\Delta\tau_i$ is the time interval in an isothermal anneal during which an irradiated sample has recovered an equivalent amount to a sample isochronally annealed at temperature T_i, c^1 is a constant, E is the activation energy and K is the gas constant. Plots of $\ln \Delta\tau_i$ versus ${}^{1}/T_i$ are shown in Figures 5, 6, 7, and 8. The calculated activation energies are as follows:

1) 50°C irradiation - 1.9 eV based on proportional limit values

2) 50°C irradiation - 1.8 eV based on yield stress values

3) 280°C irradiation - 2.1 eV based on proportional limit values

4) 280°C irradiation - 2.2 eV based on yield stress values.

This yields an average activation energy of 2.0 eV for the annealing of irradiation damage in Zircaloy-2 in the temperature range 275°C to 332°C. This activation energy is considered to be accurate to within ± 0.3 eV. More correctly, one should perhaps only consider the activation energies derived from proportional-limit values as the yield stress depends upon the rate of work hardening whereas the proportional limit does not. However, using the proportional-limit values alone, one also obtains an average value for the activation energy of 2.0 eV.

As shown in the Appendix, the order of the reaction (γ) may be determined by plotting ln ΔP versus ln (τ + M) where ΔP is a chosen increment of recovery of the proportional limit, τ is the time of isothermal annealing, and M is a value chosen to give a straight-line plot. Plots of ln ΔP versus ln (τ + M) are shown in Figures 9 and 10, the slopes (m) of which give the order of the reaction since;

$$m = {}^{1}/(1-\gamma) \qquad \text{(Equation 13 - Appendix)}$$

For the 50°C irradiation a straight line is obtained with M equal to 10; the slope of this line being - 0.48. Substituting into equation 13 a value of 3.08 (i.e. $\approx$3) is obtained for the order of reaction. It is shown in the Appendix that a plot of $(P_o - P_\infty / P_\tau - P\ )^{\gamma-1}$ versus τ should yield a straight line for a correctly determined value of γ from above. (P_o is the as-irradiated value of the proportional limit, P_∞ is the fully annealed value, and P_τ is the value after annealing for time τ). A straight line is obtained, in the 50°C irradiation case, for γ = 3 as shown in Figure 11. However, for the 280°C irradiation the nature of the results is such that it is difficult to assign any particular value of M to a straight line in the range M = 0 to M = 10. Similarly a plot of $(P_o - P_\infty / P_\tau - P_\infty)^{\gamma-1}$ versus τ for various values of γ (Figure 12) does not yield a straight line over the whole range for any of the values of γ tested, although the lower values of 2 and 3 certainly appear to be favoured over the higher values.

It appears that there is no simple interpretation of the order-of-reaction results obtained in this study. When single point defects diffuse to sinks capable of absorbing an infinite number of defects the order of reaction is unity. For the case in which different point defects annihilate each other when they combine after random migration, or in which two similar defects have greater mobility when they combine, the order of reaction is equal to two. However orders of reaction greater than two or fractional orders of reaction are difficult to interpret.

Also shown in Figures 9 and 10 are plots of ΔP versus $\tau^{1/2}$. According to Sosin and Brinkman [(3)], in any model involving random migration of an initially uniform distribution of point defects to a fixed array of infinite sinks, the dependence upon P is $\tau^{1/2}$ for sufficiently small times. In this study the ΔP versus $\tau^{1/2}$ plots do not yield straight lines over the entire time scale and insufficient data are available to determine if P is proportional to $\tau^{1/2}$ for very short times or not.

(c) Investigation of Yield-Point Phenomenon

Annealed Zircaloy-2 specimens irradiated at 280°C with 7.7 x 10^{19} n/cm^2 and tested at room temperature exhibited no sign of a yield point, this being consistent with the results of the previous study (1). Other specimens, with the same irradiation history, were tested at 280°C and their stress-strain curves exhibited a slight break in the curve in the region of the proportional limit but no pronounced yield point. Similarly, for specimens irradiated at 50°C with 9.1 x 10^{19} n/cm^2 and tested at room temperatures, there was a slight break in the stress-strain curve but no pronounced yield point. Typical stress-strain curves for the above three cases are given in Figure 13. Also shown is the curve for the same material irradiated previously (1) at 280°C with 2.7 x 10^{20} n/cm^2 in the CR-V loop and which exhibits a yield point characterized by an increase in elongation at practically constant load. It should be noted however that the samples irradiated in the CR-V loop had about 3.5 times as much exposure as samples irradiated at 280°C in the hot transformer rod.

DISCUSSION OF RESULTS

It is interesting to note that no definite yield point was developed in annealed Zircaloy-2 irradiated at 280°C and then tested at 280°C, in contrast to a previous study (1) in which evidence of a yield point was found. The material used for both investigations was identical and consequently the difference in behaviour may be attributed to the greater integrated fast flux in the earlier investigation or to slight differences in the fast neutron spectrum between the CR-V loop and the transformer rods. Kemper and Zimmerman (4) found that annealed Zircaloy-2 irradiated at 40 to 60°C with 1.4 x 10^{21} thermal neutrons/cm^2, and tested at room temperature, exhibited a yield point. This is in contrast to the present study in which no definite yield point was found in specimens irradiated at 50°C and tested at room temperature. Disagreement could be due to differences in integrated fast flux, fast neutron spectrum, or starting material.

The results on the effect of irradiation at 380°C on cold-worked and annealed Zircaloy-2 show that very little irradiation damage remains thus indicating that the point defects formed during irradiation at 380°C are being annihilated almost as quickly as they are produced. The post-irradiation annealing results for irradiated annealed Zircaloy-2 are consistent with the 380°C irradiation results as they show that very little irradiation damage remains when material irradiated at 50°C and 280°C is given 1 hour post-irradiation anneals at 375°C.

The 380°C irradiation results on cold-worked material indicate that a small amount of irradiation damage remains and that the normal thermal recovery of cold work occurring out pile at 380°C is essentially the same as that occurring during the irradiation. This suggests that the recovery of irradiation damage in Zircaloy-2 irradiated at 380°C for 41 days is occurring virtually independently from the recovery of cold work. Post-irradiation annealing results on cold-worked Zircaloy-2 (irradiated at 280°C for 128 days) obtained in the earlier study [1] also support this view. The above evidence does not completely rule out the possibility of the rate of recovery of cold work in Zircaloy-2 being affected by irradiation but does narrow the range over which such an enhancement may exist and also suggests that any effect, if present, is small.

The isochronal recovery curve for material irradiated at 280°C agrees very well with the curve obtained in the earlier study [1]. In both these cases the sharp drop in the initial portion of the recovery curves suggests that some recovery of irradiation damage is occurring during the irradiation at 280°C. Confirmation of this is provided by an examination of the isochronal recovery curve for material irradiated at 50°C in which it is apparent that some recovery of irradiation damage is occurring at temperatures as low as 250°C.

Comparing the recovery data for the 50°C and the 280°C irradiations, it can be seen that in both cases the irradiation damage anneals out in the range 250°C to 400°C and is characterized by a single activation energy of approximately 2 eV throughout this range.

One mechanism that has been proposed for irradiation hardening in metals is the segregation of point defects to dislocations. In favour of this argument is the fact that only a small number of defects is required to produce the hardening. In addition, Cottrell [5] claims that the observed shape of the stress-strain curve, the coarse slip lines, the yield drop, and the dependence of yield stress on temperature and strain rate all favour a mechanism in which the nucleation of slip, rather than the propogation of slip, is made difficult by irradiation damage. According to Cottrell [5] the fact that the irradiation hardening in copper, nickel, and iron anneals out at relatively high temperatures (225°C to 400°C) and with an activation energy for self diffusion may be due to the fact that even though the dislocation lines straighten themselves out as much as possible at lower temperatures, the hardened state persists because the nodes of the dislocation network also migrate during the absorption and straightening process. An extensive anneal is then needed to transform the dislocation network from the metastable state to the state characteristic of a fully annealed crystal, such as can be obtained only at temperatures in the range where the crystal contains an abundance of thermally-created vacancies.

Another mechanism that has been proposed for irradiation hardening is the clustering of point defects which then provide barriers for the movement of dislocations. In this case the hardening is annealed out with an energy approaching that for self diffusion since the clusters are not removed until there is a large number of thermally created vacancies.

Seeger [6] believes that irradiation hardening comes about by the thermally and stress activated cutting of dislocations through a forest of obstacles, these obstacles being the so-called disturbed "zones" in the lattice. Elimination of the hardening "zones" is considered to be possible at temperatures only at which appreciable self diffusion through the bulk of the material is possible. The activation energy of softening should be somewhat less than the activation energy of self diffusion since vacancies probably have a lower formation energy in the "zones" than at locations such as jogs in edge dislocations.

In all the above theories of irradiation hardening the activation energy for the annealing of the hardening is approximately equal or slightly less than that for self diffusion. Borisov et al[7] measured the self diffusion in alpha zirconium and report an activation energy of 22,000 cal/mole (0.95 eV) and a value of 10^{-7} cm^2/sec for the temperature-independent diffusion coefficient D_o. These values are open to question however as they were obtained from only three points on a ln D vs $^1/T$ plot. More recently, Lyashenko et al [8] have studied self diffusion in zirconium and zirconium-tin alloys. For alpha zirconium they report an activation energy for self diffusion of 52,000 calories/mole (2.25 eV) and a D_o value of 5.9×10^{-2}. For an alloy containing 1.30 weight % tin, which compares favourably with the 1.36 weight % tin in the Zircaloy-2 used in this study, they obtain an activation energy of 62,000 calories/mole (2.69 eV) and a D_o value of 5.0. These values may be questionable however as even in their work on beta zirconium, reported in the same study, they experience considerable diffusion, which cannot be attributed to volume diffusion, occurring in the beta phase at temperatures below 1000°C. Certainly the loss of creep strength in zirconium at temperatures greater than 400°C, even though zirconium has a melting point of 1830°C, seems to indicate that the self diffusion in alpha zirconium is considerably lower than a value of approximately 3 eV expected from a plot of absolute melting temperature versus self-diffusion activation energies for various metals.

Any model put forward to explain irradiation hardening in Zircaloy-2 must also account for the fact that the irradiation damage does not have a pronounced affect on the normal recovery of cold-worked materials. If the segregation of irradiation-produced point defects to dislocations alters the form of the initial dislocations one would expect the normal recovery of cold work to be altered. Consequently a model in which the pinning of dislocations by point defects produces irradiation hardening would not be consistent with the experimental data. Similarly, vacancy clusters can result in a change in the dislocation form if the clusters are carried along with the dislocation and become annihilated or form voids at the centre of the dislocation; hence irradiation hardening in Zircaloy-2 by clustering may be questionable. Seeger's model (6) of lattice hardening would be consistent with the present results as the presence of a forest of obstacles or "zones" should only make the motion of the dislocations through the lattice more difficult and should not change the initial form of the dislocations. However, in their study of irradiation hardening in copper and nickel, Makin and Minter (9) observed that although the observed temperature dependence of lattice hardening in copper and nickel was in excellent agreement with Seeger's theory (6) for material in the "as-irradiated" condition this was not true for material subjected to post-irradiation annealing treatments. Also, Makin and Minter (9) show that in addition to the lattice hardening one has to consider that dislocation locking can occur during irradiation.

Recently, Silcox and Hirsch (10) examined neutron-irradiated copper foils in an electron microscope. They claimed their observations suggest that the main features of the hardening mechanism in irradiated quenched and fatigued metals can be explained in terms of;

1) 'forest' hardening due to the presence of dislocation loops, and

2) 'source' hardening due to either initial locking of the dislocations other than loops by the formation of many jogs, or to the fact that the loops themselves may act as sources.

The irradiation hardening in copper annealed out at a temperature at which the loops disappear by climb and with an activation energy close to that for self-diffusion. A study of irradiated foils would help determine whether 'forest' hardening due to dislocation loops was occurring in Zircaloy-2 or not.

In any event, it is apparent from the analysis of irradiation data carried out in this study that it is difficult to obtain a clearer understanding of the mechanism(s) responsible for irradiation damage in Zircaloy-2 without;

1) further knowledge of some of the fundamental properties of point defects in zirconium or Zircaloy-2, and

2) observations of dislocation behaviour in irradiated thin foils using the electron microscope.

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Table 1

Room Temperature Tensile Properties of Unirradiated and Irradiated Annealed Zircaloy-2

Irradiation History		Metallurgical Condition	Prop. Limit (kips)	0.2% Offset Y.S. (kips)	U.T.S. (kips)	% Uniform Elong.	Total % Elong.
unirradiated	↓	annealed	44.8	51.2	78.5	14	24
unirrd-out pile (280°C)	↓	"	44.3	49.4	76.0	12	20
unirrd-out pile (380°C)		"	45.4	50.4	73.0	13	19
9.1×10^{19} n/cm^2 (50°C)	↓↓	"	67.0	72.0	87.2	4	13
3.6×10^{19} n/cm^2 (220°C)	↓	"	60.9	65.6	85.1	7	20
7.7×10^{19} n/cm^2 (280°C)	↓↓	"	63.3	66.6	86.1	5	16
2.7×10^{20} n/cm^2 (280°C)	↓	"	75.7	79.3	91.4	4	13
9.5×10^{19} n/cm^2 (380°C)		"	49.4	55.8	76.4	9	18

↓ previous results from CRMet-827 (1)

results listed represent the average of 6 samples tested in each of the above conditions except where marked with ↓↓; in which case result is average of 2 samples

the 280°C irradiation with 2.7×10^{20} n/cm^2 was performed in the CR-V loop; all other irradiations were performed in either low or high temperature transformer rods

the out-pile heat treatments were carried out for the same lengths of time as the corresponding irradiations at the same temperature i.e. 128 days at 280°C and 41 days at 380°C.

Table 2

Room Temperature Tensile Properties of Irradiated and Unirradiated Cold-Worked Zircaloy-2

Irradiation History	Metallurgical Condition	Prop Limit (kips)	0.2% Offset Y.S. (kips)	U.T.S. (kips)	% Uniform Elong.	Total % Elong.
unirradiated †	13.1% c.w.	84.1	88.1	92.9	3	14
unirrd-out pile (280°C) †	"	70.5	74.5	84.3	4	12
unirrd-out pile (380°C)	"	59.0	62.4	77.8	8	15
3.6 x 10^{19}n/cm^2(220°C)†	"	85.8	90.5	96.7	2	10
2.7 x 10^{20}n/cm^2(280°C)†	"	98.1	102.0	104.1	1	9
9.5 x 10^{19}n/cm^2(380°C)	"	61.7	67.4	82.8	6	16
unirradiated †	tempered	72.6	77.1	92.5	6	16
unirrd-out pile (280°C) †	25.5% c.w.††	70.0	76.0	90.0	6	13
unirrd-out pile (380°C)	"	62.4	65.7	81.8	7	11
3.6 x 10^{19}n/cm^2(220°C) †	"	83.7	88.1	99.0	3	12
2.7 x 10^{20}n/cm^2(280°C) †	"	95.1	99.4	105.8	3	9
9.5 x 10^{19}n/cm^2(380°C)	"	62.6	67.8	84.4	5	15

† previous results from CRMet-827[1]

†† tempering treatment was 15 minutes at 425°C

results listed represent the average of 6 samples tested in each of the above conditions

the out-pile heat treatments were carried out for the same lengths of time as the corresponding irradiations at the same temperature i.e. 128 days at 280°C and 41 days at 380°C.

Table 3

Post-Irradiation Annealing Results for Annealed Zircaloy-2

Irradiated at 50°C with 9.1×10^{19} n/cm^2

A. Isochronal Anneals (1 hour at various temperatures)

Annealing Temperature (°C)	Prop Limit (kips)	0.2% Offset Y.S. (kips)	U.T.S. (kips)	% Uniform Elong.	Total % Elong.
irradiated	67.0	72.0	87.2	4	13
150	67.0	72.0	87.0	4	13
250	66.2	71.0	84.5	4	13
280	63.1	68.5	85.0	5	14
300	58.3	63.5	81.8	6	20
312	57.4	61.5	83.0	7	16
325	54.2	58.5	78.5	7	16
337	47.0	52.5	74.5	10	18
350	44.8	49.8	69.7	10	18
375	44.5	49.5	74.0	11	19
400	44.0	48.0	72.2	12	22

B. Isothermal Anneals (various times at 325°C)

Annealing Time (minutes)	Prop Limit (kips)	0.2% Offset Y.S. (kips)	U.T.S. (kips)	% Uniform Elong.	Total % Elong.
irradiated	67.0	72.0	87.2	4	13
5	63.3	69.1	86.0	5	14
10	61.0	67.0	85.0	6	23
20	57.4	62.5	84.0	7	16
40	55.5	60.0	83.5	9	22
60	54.2	58.5	78.5	7	16
140	51.0	56.0	81.0	12	24

All the specimens were tested at room temperature.

Table 4

Post-Irradiation Annealing Results for Annealed Zircaloy-2

Irradiated at 280°C with 7.7 x 10^{19} n/cm^2

A. Isochronal Anneals (1 hour at various temperatures)

Annealing Temperature (°C)	Prop Limit (kips)	0.2% Offset Y.S. (kips)	U.T.S. (kips)	% Uniform Elong.	Total % Elong.
irradiated	63.3	66.6	86.1	5	16
290	62.0	66.0	85.8	6	17
300	60.0	65.0	83.0	7	17
312	58.0	63.0	83.1	5	16
325	56.0	61.5	82.5	10	24
332	53.0	59.0	79.5	11	21
337	50.5	57.0	79.6	11	20
350	47.8	53.7	79.1	13	24
375	46.1	52.5	78.0	11	23
400	47.0	52.0	77.9	14	26

B. Isothermal Anneals (various times at 325°C)

Annealing Time (minutes)	Prop Limit (kips)	0.2% Offset Y.S. (kips)	U.T.S. (kips)	% Uniform Elong.	Total % Elong.
irradiated	63.3	66.6	86.1	5	16
5	62.0	65.5	85.0	5	15
10	59.5	64.5	84.0	6	19
20	58.2	63.5	85.3	8	20
40	57.0	62.5	83.5	9	18
60	56.0	61.5	82.5	10	24
140	54.0	59.0	80.5	12	23

All the specimens were tested at room temperature

Appendix

Analysis of Post-Irradiation Annealing Data

If the rate of annealing of excess defects produced by irradiation damage obeys the chemical rate equation, one can write the following:

$$dn/dt = - f(n, q_1, q_2 \ldots q_n) \exp(^{-E}/KT) \qquad (1)$$

where n is the excess defect concentration, t is the time of annealing, T is the absolute temperature, K is the gas constant, E is the activation energy associated with the process, and f(n,q) is a function of the defect concentration (n) and other variables (q_1, $q_2 \ldots q_n$) independent of t and T. If the relationship between a measured property P and n is a single-valued monotonically increasing or decreasing function independent of t, T, and q_1, $q_2 \ldots q_n$ we can write:

$$dp/dt = - F(p, q_1, q_2) \exp(^{-E}/KT) \qquad (2)$$

The activation energy for recovery of irradiation damage can be obtained by comparing the recovery occurring during an isothermal anneal with that occurring during an isochronal anneal. Consider the isochronal curve shown in Figure A and let P_o be the initial value of P (as-irradiated), P_i be the measured value of P after annealing at temperature T_i for a constant time interval Δt_i, and P_∞ be the fully annealed value. Applying equation (2) to the isochronal case one obtains:

$$\int_{P_o}^{P_i} dP/F(p,q) = \int_{t_o}^{t_i} \exp - {}^{E}/KT_i \; dt \qquad (3)$$

Now consider an isothermal curve (Figure B) where specimens of identical irradiation history have been annealed at a temperature T_a for various periods of time τ. At a point corresponding to P_i there will be a time τ_i and hence for isothermal annealing one can write:

$$\int_{P_o}^{P_i} dP/F(p,q) = \int_{\tau_o}^{\tau_i} \exp(^{-E}/KT_a) \, d\tau \qquad (4)$$

The left hand side of equations 3 and 4 are equal hence;

$$\int_{t_o}^{t_i} \exp(^{-E}/KT_i) \, dt = \int_{\tau_o}^{\tau_i} \exp(^{-E}/KT_a) \, d\tau \qquad (5)$$

Integrating, one obtains;

$$\Delta\tau_i = \Delta t_i \exp(^-E/KT_a) \exp(^-E/KT_i) \qquad (6)$$

where $\Delta\tau_i = \tau_i - \tau_o$ and $\Delta t_i = t_i - t_o$

Since $\Delta t_i \exp(^-E/KT_a)$ is a constant, equation 6 may be rewritten as;

$$\Delta\tau_i = c \exp(^-E/KT_i) \qquad (7)$$

Taking logarithims of both sides yields;

$$\ln \Delta\tau_i = c^1 - {}^E/KT_i \qquad (8)$$

If the recovery resulting from annealing in a given temperature interval is characterized by a single activation energy a plot of $\Delta\tau_i$ against $^1/T_i$ will yield a straight line in this temperature interval.

The above method is a slight modification of the technique used in analysing electrical resistivity measurements. In the electrical resistivity case a single specimen is used to obtain an isochronal curve and another specimen of identical irradiation history is used to obtain an isothermal curve and one compares the recovery $P_i - P_{i-1}$ occurring in the isochronal anneal to the same amount of recovery occurring in the isothermal anneal during the time interval $\tau_i - \tau_{i-1}$; where P_i is the measured value of P after the ith pulse and P_{i-1} the measured value of P after the (i-1) th pulse. In the present study each point on the recovery curves represents a different specimen, but with the same irradiation history, and it is the recovery $P_o - P_i$ which one is concerned with.

If the recovery obeys a chemical rate equation, the annealing of defects during an isothermal anneal may be expressed as follows;

$$^{dn}/d\tau = -K n^\gamma \qquad (9)$$

where γ is the order of the reaction. Integration of equation 9 gives;

$$n^{(1-\gamma)} = c_1 (\tau + M) \qquad (10)$$

In the above equation;

$$c_1 = K(\gamma - 1), \qquad (11)$$

and

$$M = n_o^{(1-\gamma)}/c_1 \qquad (12)$$

where n_o is the value of n at $\tau = o$. (as-irradiated value). By plotting ln ΔP versus ln $(\tau + M)$ and choosing a value of M such that the plot is a straight line, the order of the reaction γ can be obtained from measuring the slope m of the straight line since;

$$m = 1/(1-\gamma) \qquad (13)$$

According to Piercy [1], the equation governing the mobility of point defects is as follows:

$$dn/d\tau = \nu \exp(S_m/K)\,(Z-1)\,n^{\gamma} \exp(-E_m/KT) \qquad (14)$$

where ν is the vibration frequency of the Z atoms adjacent to the defect, E_m and S_m are the energy and entropy respectively for the defect to make one lattice jump, and γ is the order of the reaction. Integrating equation 14 for $\gamma \neq 1$ one obtains;

$$(n_o/n_\tau)^{\gamma-1} = W\tau + 1, \qquad (15)$$

where n_o and n_τ are the concentration of defects initially and after annealing for time τ respectively and W is a constant if γ is a constant throughout the anneal. The value of γ obtained from equation 13 can thus be checked more accurately by plotting $(P_o - P_\infty / P_\tau - P_\infty)^{\gamma-1}$ versus τ since

$$(P_o - P_\infty / P_\tau - P_\infty)^{\gamma-1} = W\tau + 1$$

where P_o is the as-irradiated value of the proportional limit, P_∞ is the fully annealed value, and P_τ is the value after annealing for time τ.

REFERENCES

1. Piercy, G. R. - AECL - CRMet-782 - June (1958) - "Point Defects in Platinum".

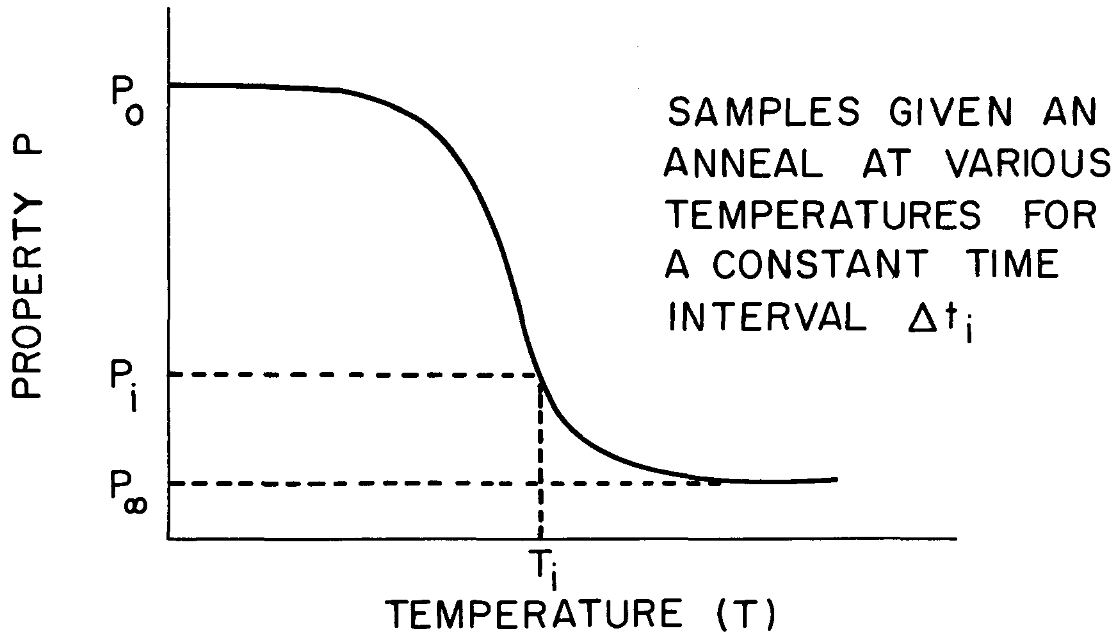


FIGURE A: ISOCHRONAL ANNEALING CURVE

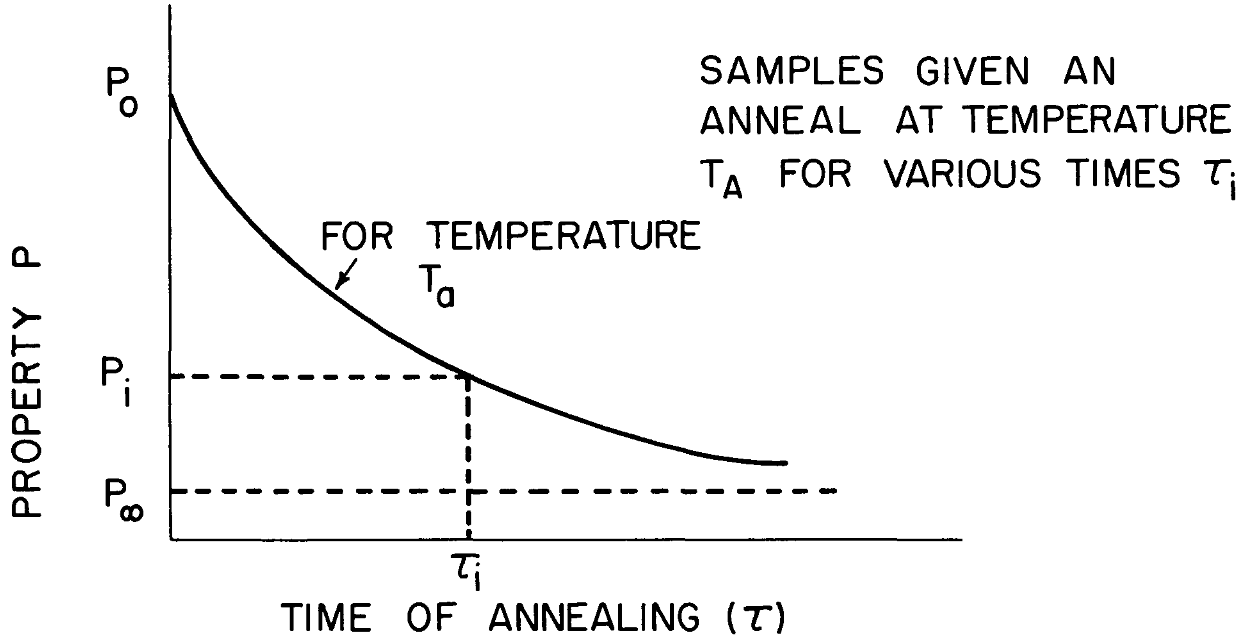


FIGURE B: ISOTHERMAL ANNEALING CURVE

FIGURE I

ISOCHRONAL RECOVERY CURVES FOR ANNEALED ZIRCALOY-2 IRRADIATED AT 50 °C

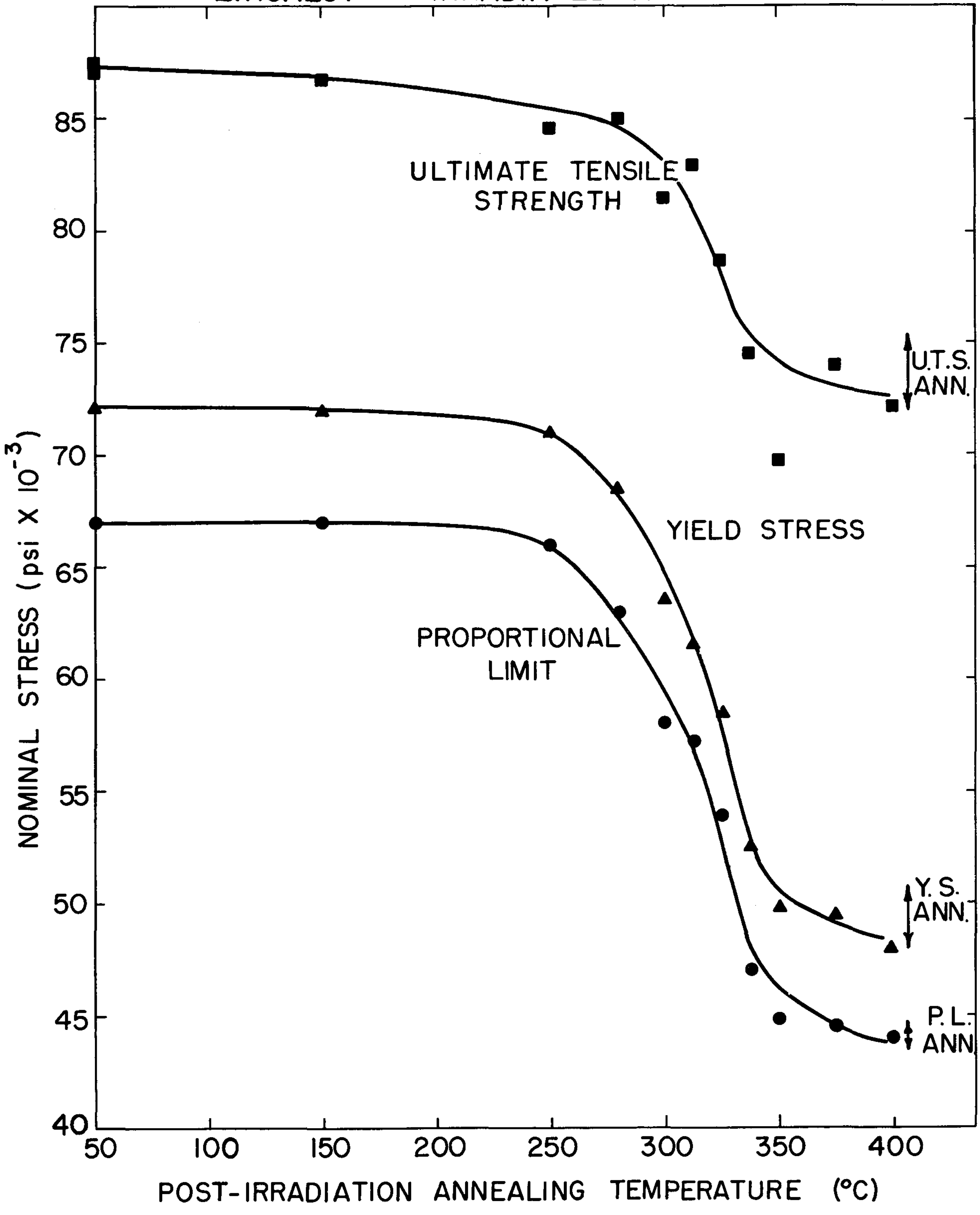


FIGURE 2
ISOCHRONAL RECOVERY CURVES FOR ANNEALED ZIRCALOY-2 IRRADIATED AT 280 ° C

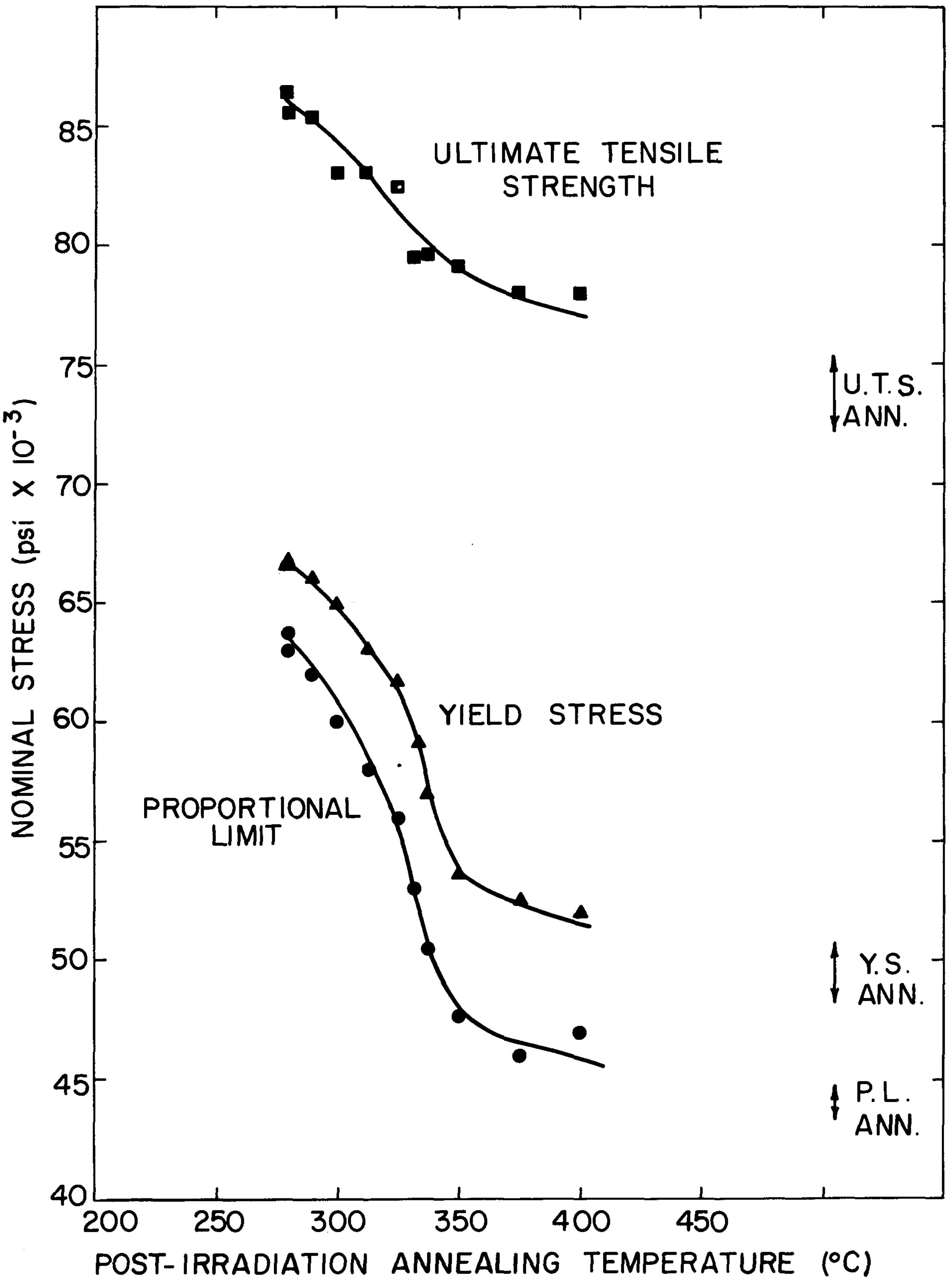


FIGURE 3
ISOTHERMAL RECOVERY CURVES FOR ANNEALED ZIRCALOY-2 IRRADIATED AT 50°C

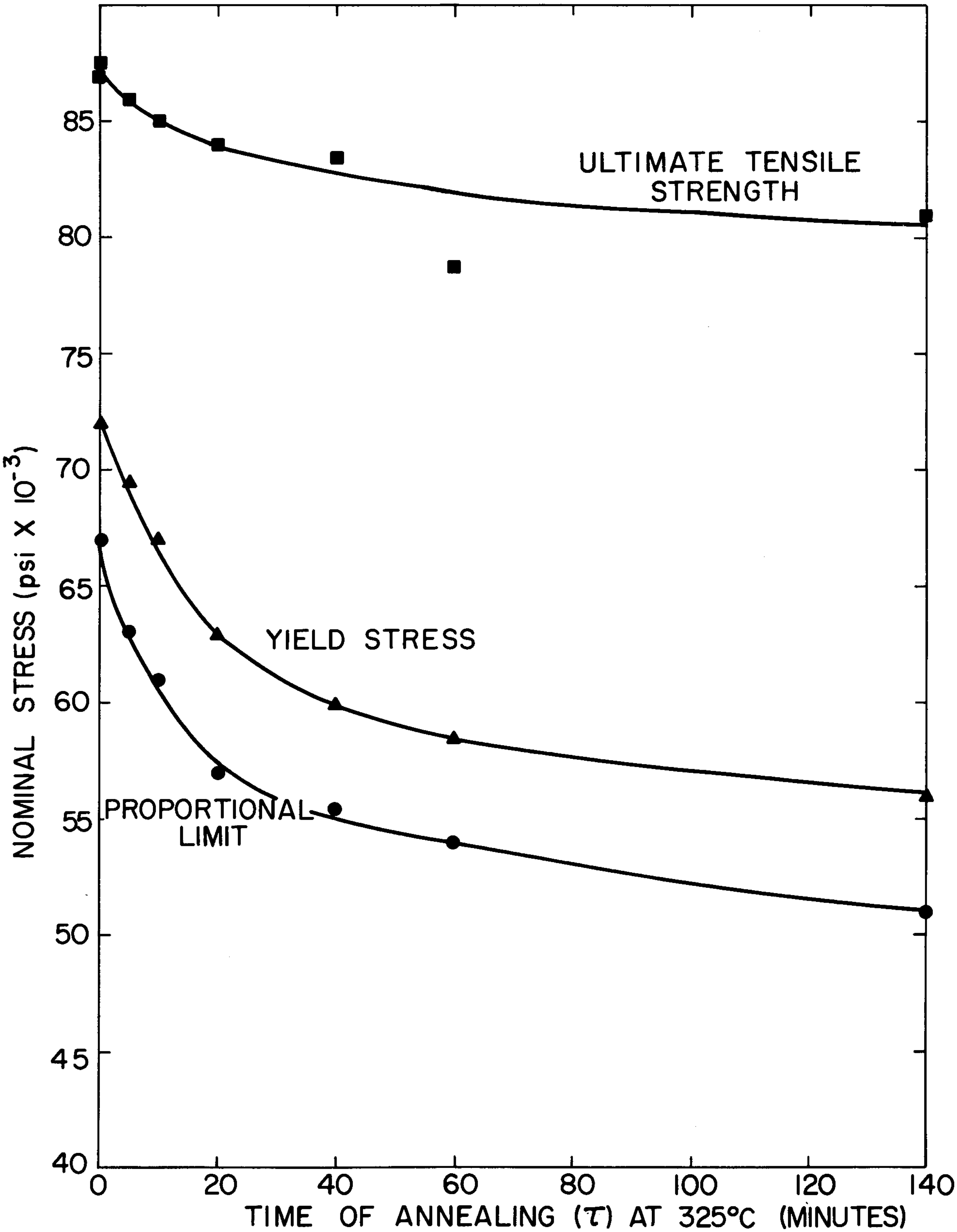


FIGURE 4
ISOTHERMAL RECOVERY CURVES FOR ANNEALED ZIRCALOY-2 IRRADIATED AT 280°C

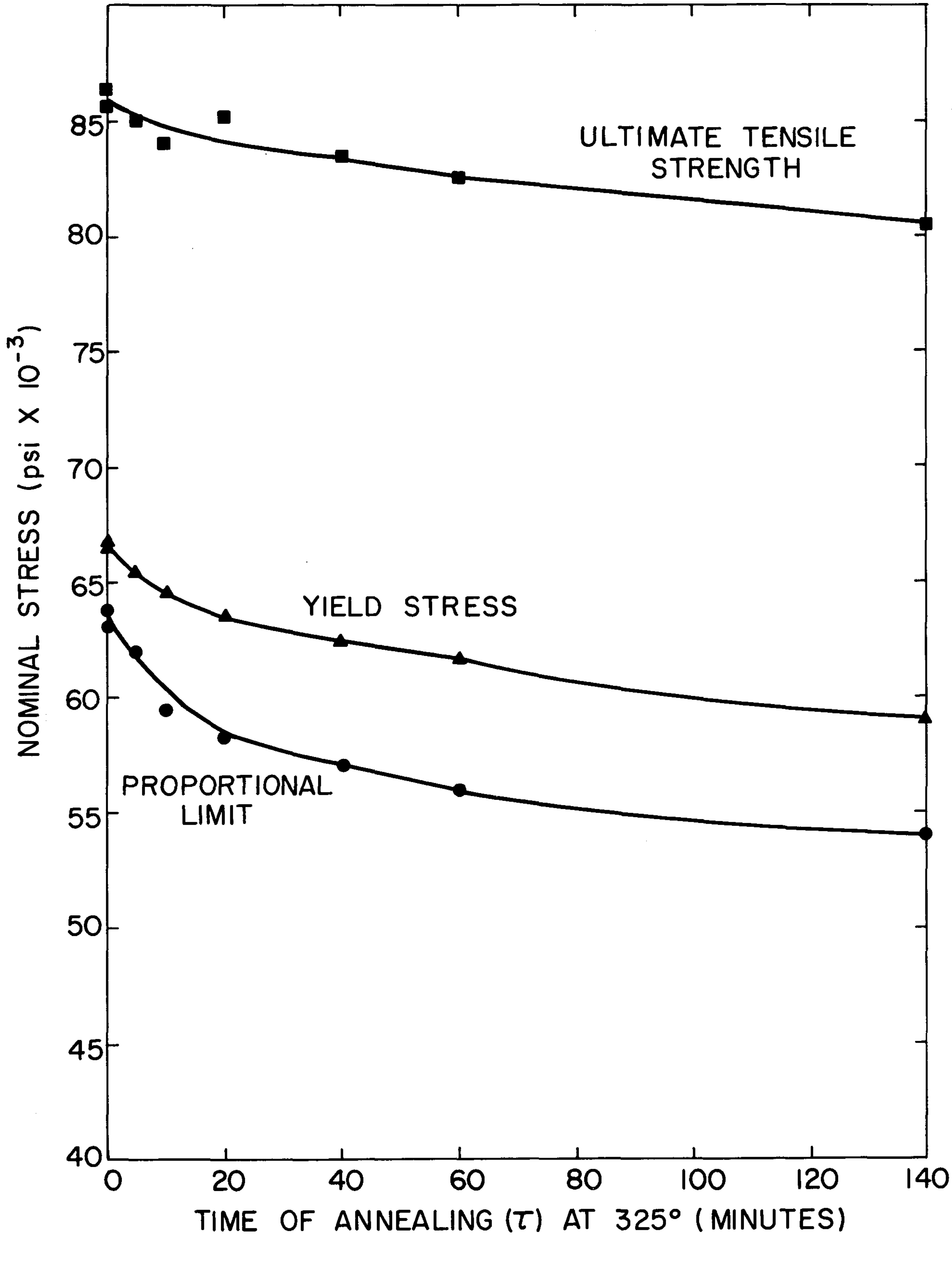


FIGURE 5

PLOT OF $\ln\Delta\tau$ vs $1/T_i$ FOR RECOVERY OF ANNEALED ZIRCALOY-2 IRRADIATED AT 50°C WITH 9.1×10^{19} n/cm^2

(DATA FOR RECOVERY OF P.L.)

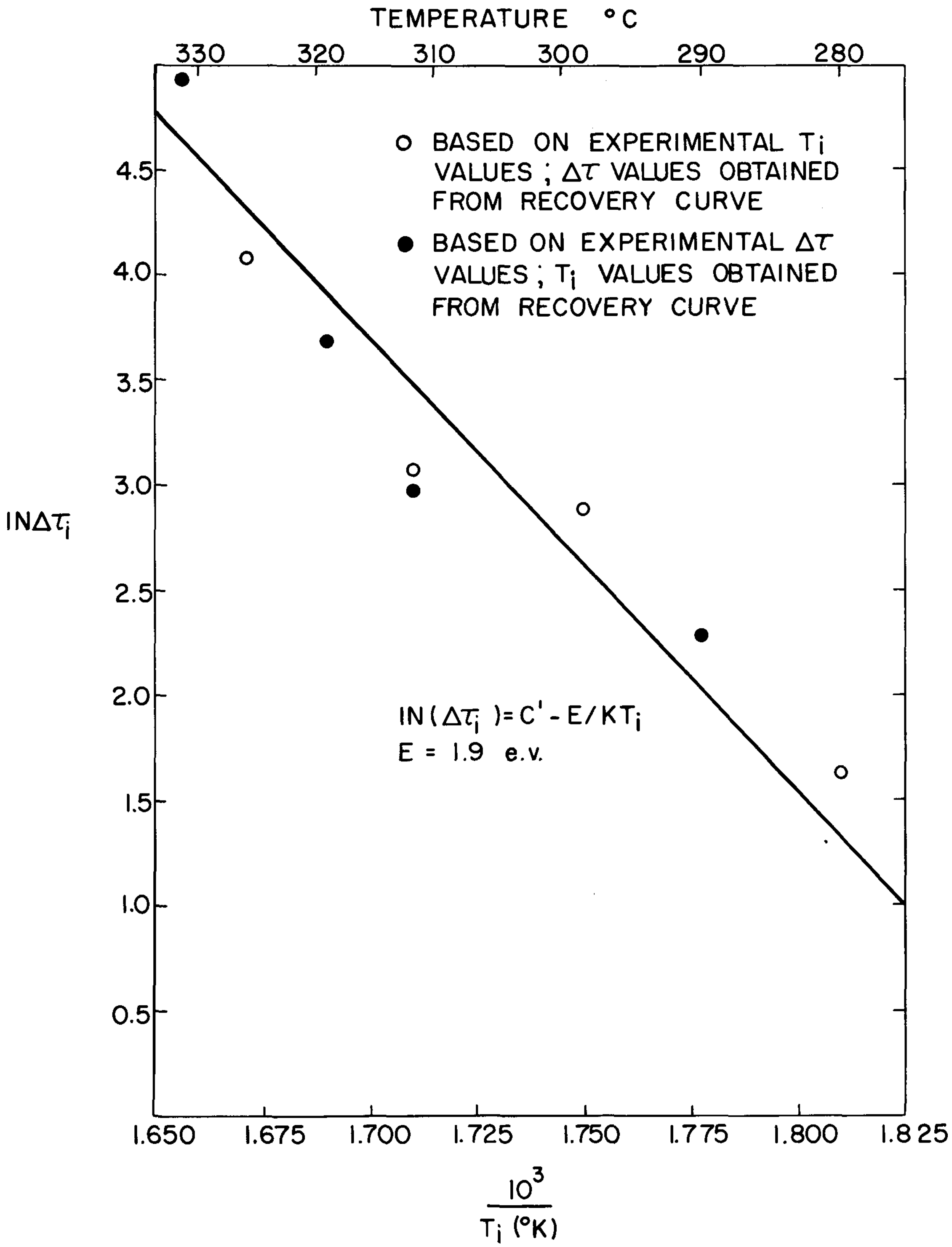


FIGURE 6

PLOT OF $\ln\Delta\tau$ vs $1/T_i$ FOR RECOVERY OF ANNEALED ZIRCALOY-2 IRRADIATED AT 50°C WITH 9.1×10^{19} n/cm^2

(DATA FOR RECOVERY OF Y.S.)

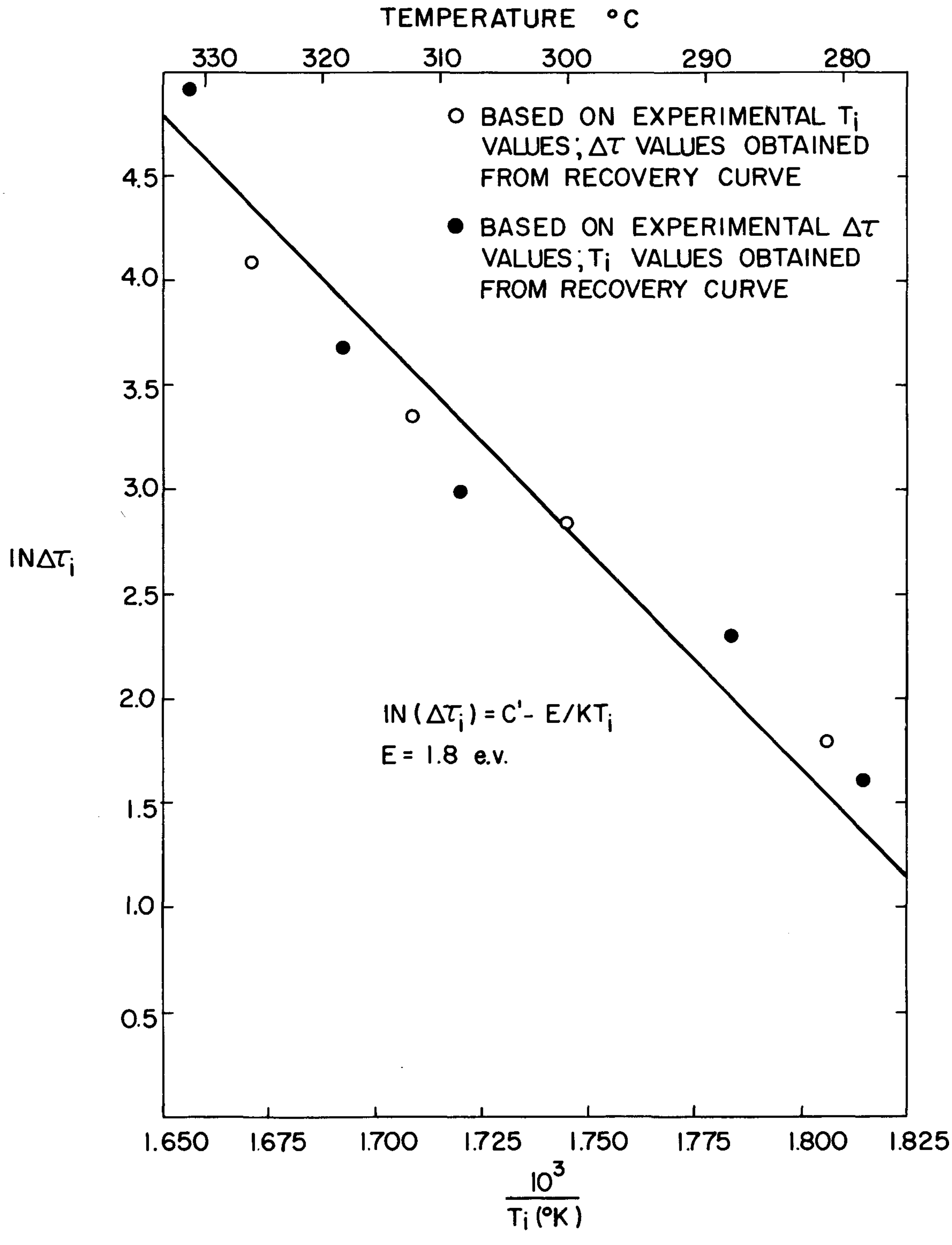


FIGURE 7

PLOT OF IN$\Delta\tau$ vs $1/T_i$ FOR RECOVERY OF ANNEALED ZIRCALOY-2 IRRADIATED AT 280°C WITH 7.7×10^{19} n/cm^2 (DATA FOR RECOVERY OF P.L.)

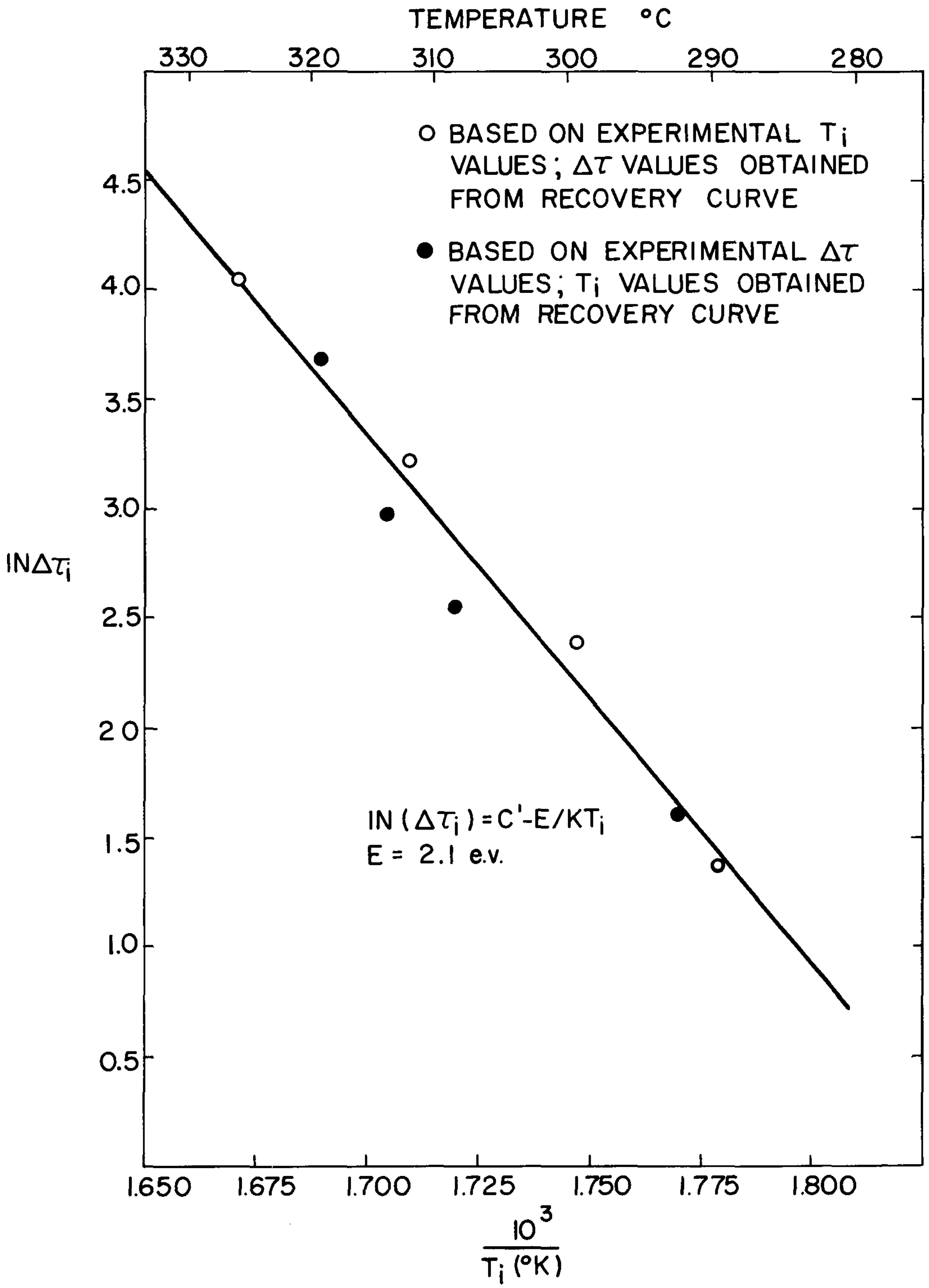


FIGURE 8

PLOT OF $\ln\Delta\tau$ vs $1/T_i$ FOR RECOVERY OF ANNEALED ZIRCALOY - 2 IRRADIATED AT 280°C WITH 7.7 X 10^{19} n/cm^2 (DATA FOR RECOVERY OF Y.S.)

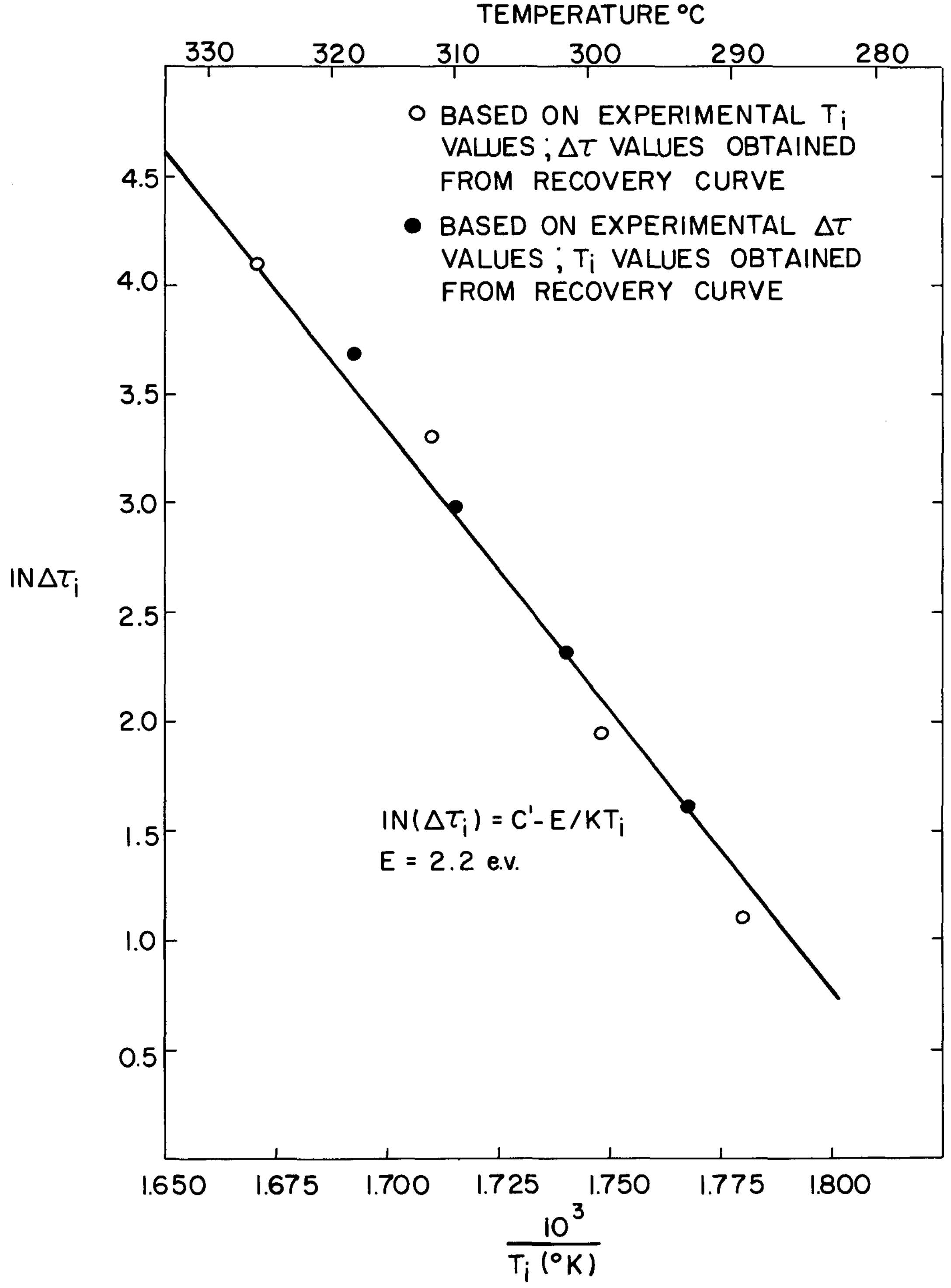


FIGURE 9

AN ANALYSIS OF THE ISOTHERMAL RECOVERY DATA FOR ANNEALED ZIRCALOY-2 IRRADIATED AT 50°C

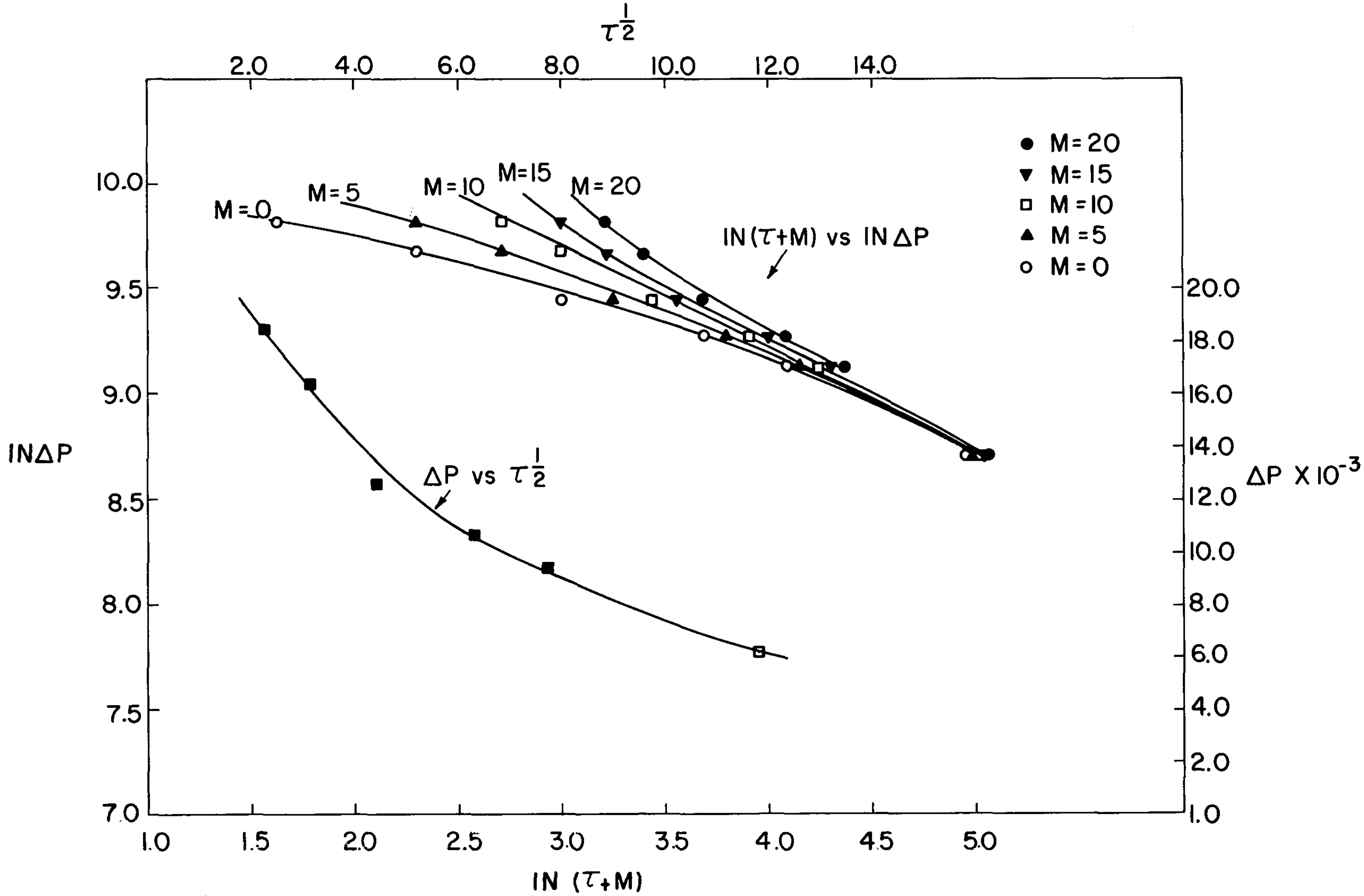
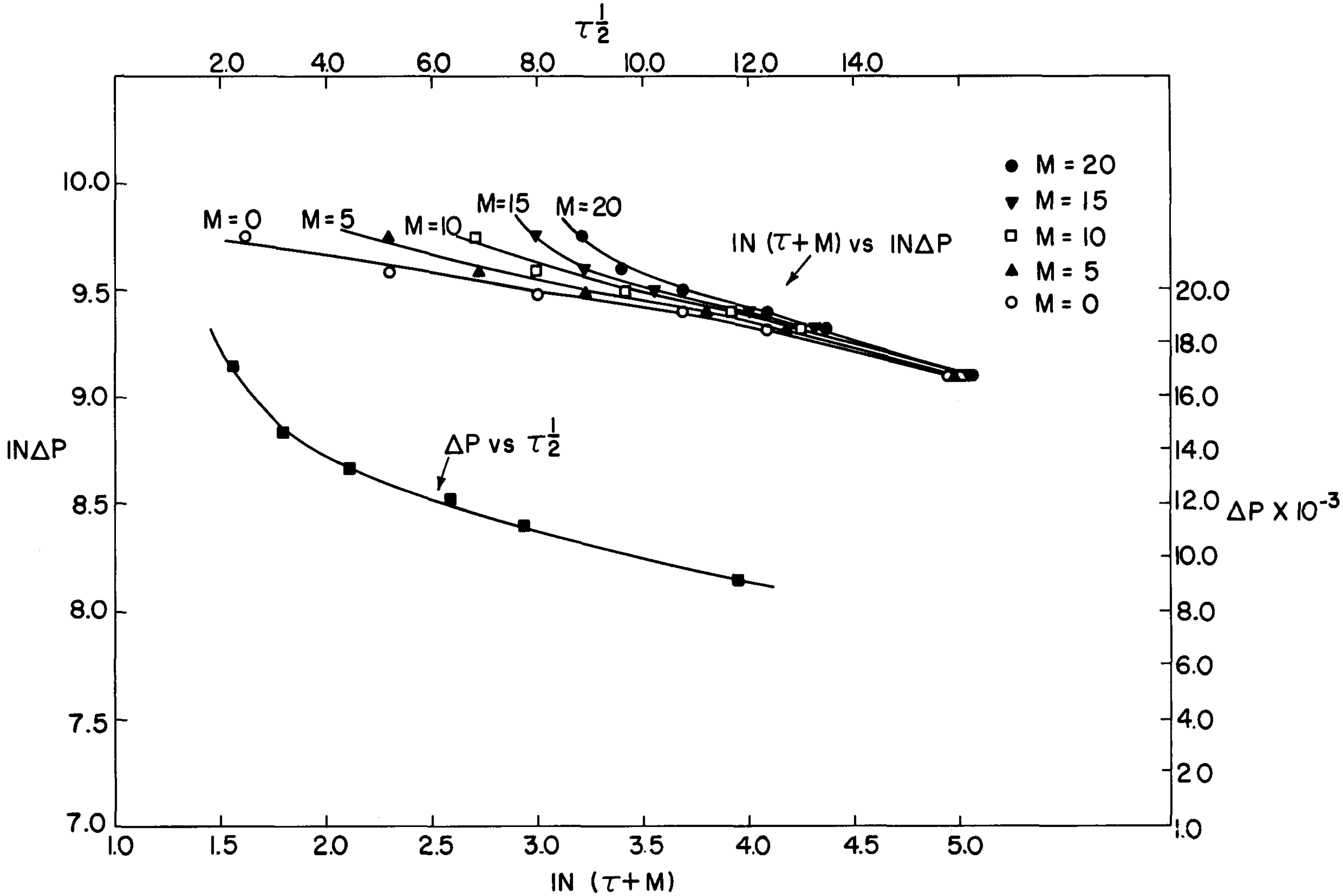


FIGURE 10

AN ANALYSIS OF THE ISOTHERMAL RECOVERY DATA FOR ANNEALED ZIRCALOY-2 IRRADIATED AT 280 °C



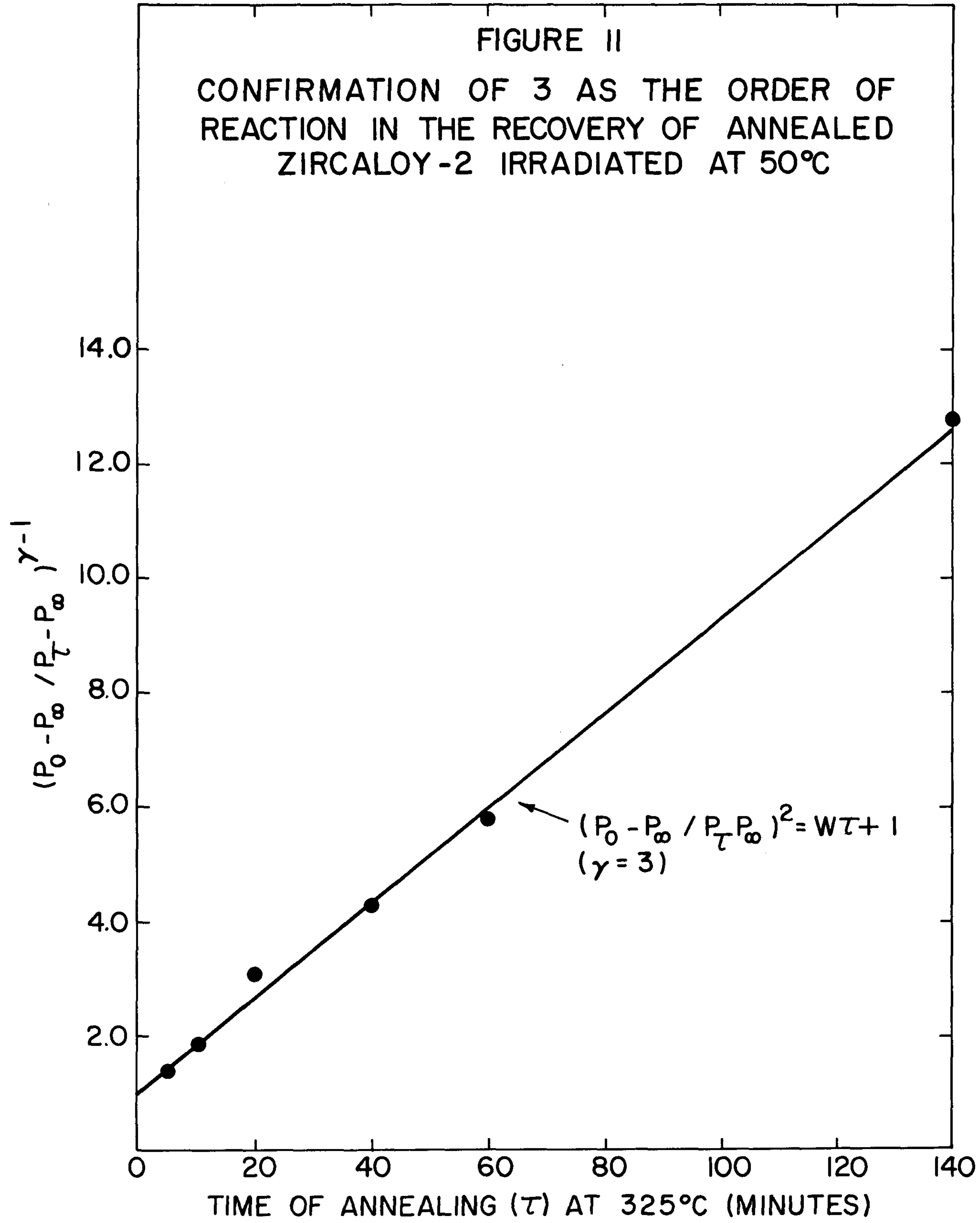


FIGURE 11

CONFIRMATION OF 3 AS THE ORDER OF REACTION IN THE RECOVERY OF ANNEALED ZIRCALOY-2 IRRADIATED AT 50°C

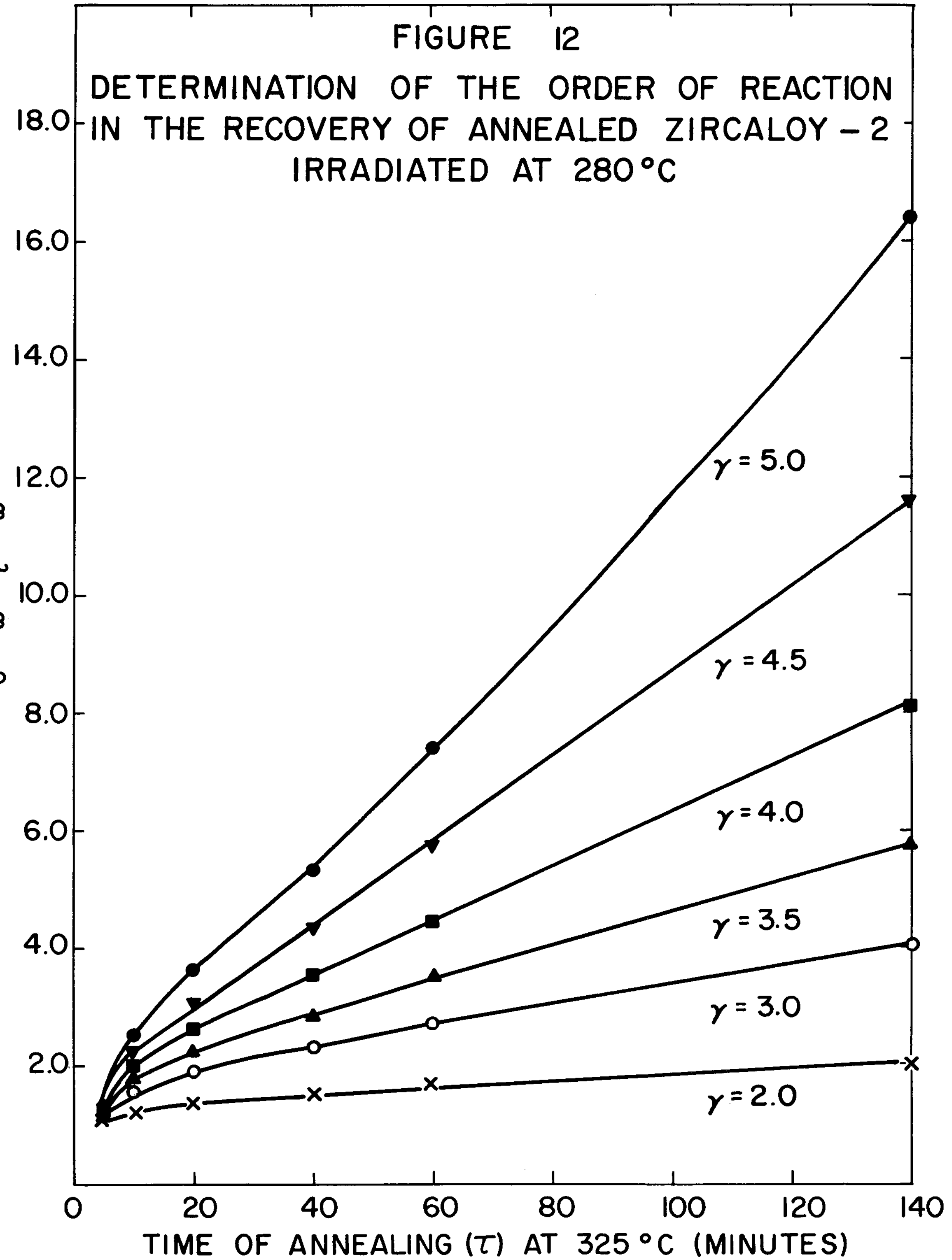


FIGURE 12
DETERMINATION OF THE ORDER OF REACTION IN THE RECOVERY OF ANNEALED ZIRCALOY – 2 IRRADIATED AT 280°C
$(P_0 - P_\infty / P_\tau - P_\infty)^{\gamma - 1}$
18.0
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0
20
40
60
80
100
120
140
TIME OF ANNEALING (τ) AT 325°C (MINUTES)
γ = 5.0
γ = 4.5
γ = 4.0
γ = 3.5
γ = 3.0
γ = 2.0

FIGURE 13

STRESS-STRAIN CURVES FOR IRRADIATED ANNEALED ZIRCALOY-2