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POST-IRRADIATION RECOVERY OF GROWTH IN ZIRCALOY

(AWBA Development Program)

DECEMBER 1977

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BETTIS ATOMIC POWER LABORATORY
WEST MIFFLIN, PENNSYLVANIA

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ZIRCALOY**
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C. C. Dollins

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FOREWORD

The Shippingport Atomic Power Station located in Shippingport, Pennsylvania was the first large-scale, central-station nuclear power plant in the United States and the first plant of such size in the world operated solely to produce electric power. This project was started in 1953 to confirm the practical application of nuclear power for large-scale electric power generation. It has provided much of the technology being used for design and operation of the commercial, central-station nuclear power plants now in use.

Subsequent to development and successful operation of the Pressurized Water Reactor in the AEC-owned reactor plant at the Shippingport Atomic Power Station, the Atomic Energy Commission in 1956 undertook a research and development program to design and build a light Water Breeder Reactor core for operation in the Shippingport Station. In 1976, with fabrication of the Light Water Breeder Reactor (LWBR) nearing completion the Energy Research and Development Administration established the Advanced Water Breeder Applications program (AWBA) to develop and disseminate technical information which would assist U.S. industry in evaluating the LWBR concept. All three of these reactor development projects have been administered by the Division of Naval Reactors with the goal of developing practical improvements in the utilization of nuclear fuel resources for generation of electrical energy using water-cooled nuclear reactors.

The objective of the Light Water Breeder Reactor project has been to develop a technology that would significantly improve the utilization of the nation's nuclear fuel resources employing the well-established water reactor technology. To achieve this objective, work has been directed toward analysis, design, component tests, and fabrication of a water-cooled, thorium oxide fuel cycle breeder reactor to install and operate at the Shippingport Station. Operation of the LWBR core in the Shippingport Station started in the Fall of 1977 and is expected to be completed in about 3 to 4 years. Then the fissionable fuel inventory of the core will be measured. This effort, when completed in about 2 to 3 years after completion of LWBR core operation, is expected to confirm that breeding actually took place.

The advanced Water Breeder Applications (AWBA) project was initiated to develop and disseminate technical information that will assist U.S. industry in evaluating the LWBR concept for commercial-scale applications. The project will explore some of the problems that would be faced by industry in adapting technology confirmed in the LWBR program. Information to be developed includes concepts for commercial-scale prebreeder cores which will produce uranium-233 for light water breeder cores while producing electric power, improvements for breeder cores based on the technology developed to fabricate and operate the Shippingport LWBR core, and other information and technology to aid in evaluating commercial-scale application of the LWBR concept.

Technical information developed under the Shippingport, LWBR, and AWBA projects has been and will continue to be published in technical memoranda, one of which is this present report.

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NOMENCLATURE

<u>Symbol</u>	<u>Definition</u>
b	Burgers vector = $3.23 \text{ \AA}$
C_o	Thermal equilibrium vacancy concentration
C_v	Concentration of vacancies in atom fraction
D_v	Vacancy diffusion coefficient = $10^{-2} \exp(-27\,660/RT)$
E_b	Binding energy between a vacancy and a depleted zone
E_t	Vacancy formation energy = 1.2 eV ($27\,660 \text{ cal/mole}$)
f	Texture factor
k	Boltzmann's constant
k_v	Grain boundary sink strength
N	Depleted zone density
N_L	Interstitial dislocation loop density
N_o	Number of lattice sites/cm ³ = $4.2 \times 10^{22}/\text{cm}^3$
n	Number of vacancies in a zone
r	Average radius of a depleted zone
r_1	$(\pi\rho)^{-\frac{1}{2}}$ = one half the distance between dislocations
r_L	Interstitial dislocation loop radius
T	Temperature
t	Time
v_c	Climb velocity of straight dislocations
α	Fraction of depleted zones that are voids
β	Grain radius
γ	Surface energy
δ	$\exp(-r_L/r_1)$ and is a weighting factor determining whether a loop is treated as a small dislocation loop with no interstitial bias or a straight dislocation with a bias
ϵ	Total strain in a polycrystalline specimen

$\dot{\epsilon}_d$	Strain rate in the basal plane caused by the climb of straight dislocations
$\dot{\epsilon}_g$	Strain rate in the basal plane caused by vacancy absorption at grain boundaries
ϵ_ℓ	Strain in the basal plane caused by interstitial loops
ϵ_p	Total strain in the basal plane
ϵ_n	Strain normal to the basal plane
μ	Shear modulus = 3.45×10^{11} dynes/cm ²
ν	Poisson's constant
ρ	$\rho_o + 2\pi r_\ell N_\ell(1 - \delta)$ = effective straight dislocation density
ρ_o	Density of dislocations not associated with loops
Ω	Atomic volume

The previously reported model for fast neutron induced growth in Zircaloy has been modified to predict post-irradiation recovery of the growth. The predicted results are compared to growth recovery data obtained by Adamson. Agreement is good if the binding energy between vacancies and depleted zones is reduced from the in-pile value of 1.1 eV to a post-irradiation value of 1.0 eV. Such a reduction is reasonable.

POST-IRRADIATION RECOVERY OF GROWTH IN ZIRCALLOY (AWBA Development Program)

C. C. Dollins

I. INTRODUCTION

Zircaloy is the prime cladding used in pressurized water nuclear reactors to separate the nuclear fuel from the coolant. Zircaloy has a close packed hexagonal lattice structure. When it is formed into a clad it has a preferred orientation texture. The basal planes of the structure line up in the direction of extension during the forming process. During fast neutron irradiation, Zircaloy grows in the direction parallel to the basal plane and shrinks in the direction normal to the basal plane.

Recently a quantitative model was developed for growth in Zircaloy⁽¹⁾. The model is based on the production by fast neutrons of depleted zones, vacancies, and interstitials. The model assumes the initial formation of $1 \times 10^{15}/\text{cm}^3$ single atom interstitial loops for both cold worked and annealed material and follows their subsequent growth into larger loops by net absorption of interstitials. The model calculates the density of depleted zones, the rate of straight dislocation climb, the rate at which point defects migrate to grain and subgrain boundaries, and the rate of recombination of point defects. The growth in the basal plane is the sum of the growth due to the formation of dislocation loops, the straight dislocation climb, and the net absorption of interstitials by the grain and subgrain boundaries.

The present work considers the recovery of growth during a post-irradiation annealing process. Recovery predictions from the model are compared to experimental results obtained by Adamson⁽²⁾.

II. THEORY

The in-pile growth model was described in the previous work⁽¹⁾ and will not be discussed here. During a post-irradiation anneal there is no ir-

radiation induced generation of vacancies or interstitials. Since the formation energy of interstitials is very large they are not thermally produced in any significant numbers and their concentration will go to zero. In-pile, the interstitial concentration is predicted to be about $1 \times 10^8/\text{cm}^3$. During an anneal these interstitials migrate to sinks. Since the loop density is on the order of $10^{15}/\text{cm}^3$ it is predicted that the interstitials have no effect and can be ignored. Vacancies will be thermally emitted from the structural defects in great numbers during an anneal, and, consequently, their concentration must be followed. The change in the vacancy concentration with respect to time is given by⁽¹⁾

$$\begin{aligned} \frac{dC_v}{dt} = & - \frac{2\pi D_v}{\ln(r_l/b)} \left\{ (C_v - C_0)\rho_0 \right. \\ & + (1 - \delta)N_L 2\pi r_L \left[C_v - C_0 \right. \\ & \left. \left. \exp \left(- \frac{\mu b \Omega \ln(32 r_L/b)}{4\pi(1 - \nu)r_L kT} \right) \right] \right\} \\ & - 84 \pi r_L N_L D_v \frac{\pi}{\ln(8r_L/b)} \left[C_v - C_0 \right. \\ & \left. \exp \left(- \frac{\mu b \Omega \ln(32 r_L/b)}{4\pi(1 - \nu)r_L kT} \right) \right] \\ & + 4\pi r_L N D_v \left\{ C_0 \exp[(E_i - E_b)/kT] - C_v \right\} \\ & - \frac{3 k_v D_v}{\beta} (C_v - C_0) \end{aligned} \quad (1)$$

The symbols are defined in the Nomenclature table. The first term on the right-hand side of Equation (1) is the loss rate of vacancies to straight dislocations, the second term is the loss rate to interstitial loops, the third term is the loss rate to depleted zones, and the fourth term is the loss rate to

grain boundaries. The sink strength of the grain boundary term is given by ⁽¹⁾

$$k_v = \left\{ \frac{2\pi}{\ln(r_1/b)} \left[\rho_0 + (1 - \delta) N_L 2\pi r_L \right] + \frac{84 \pi^2 r_L N_L}{\ln(8r_L/b)} + 4 \pi r N \right\}^{1/2} \quad (2)$$

With knowledge of the vacancy concentration it is possible to calculate the annealing rate of the depleted zones and of the interstitial dislocation loops.

The vacancy emission rate from a depleted zone in number of vacancies per second is given by ⁽¹⁾

$$\frac{dn}{dt} = -4\pi r N_0 D_v [C_0 \exp[(E_i - E_b)/kT] - C_v] \quad (3)$$

where N_0 is the number of lattice sites per unit volume and n is the number of vacancies in a zone. In the previous work it was defined that $\alpha (=0.25)$ is the fraction of the depleted zones that are in the form of voids, with the remainder of the zones in the form of relaxed vacancy disks or vacancy dislocation loops. The relation between n and loop radius, r , is

$$n\Omega = \pi r^2 b \quad (4)$$

where b is the Burgers vector of the loop. The change in radius of the loop with time is given by

$$\begin{aligned} \frac{dr}{dt} &= \frac{\Omega}{4\pi r^2} \frac{dn}{dt} \\ &= -\frac{2D_v}{b} [C_0 \exp[(E_i - E_b)/kT] - C_v] \quad (5) \end{aligned}$$

Since the majority of the depleted zones are presumably in the form of loops, Equation (5) can be used for both loops and voids with little loss in accuracy and great savings in computational time.

The net flux of vacancies into the much larger interstitial loops is given by ⁽¹⁾

$$\begin{aligned} J &= 4\pi^2 r_L (1 - \nu) D_v \frac{N_0}{\ln(r_1/b)} [C_v - C_0] \\ &\quad \exp \left(-\frac{\mu b \Omega \ln(32 r_L/b)}{4\pi(1 - \nu) r_L kT} \right) \\ &\quad + \frac{48 \pi^2 r_L D_v N_0}{\ln(8r_L/b)} [C_v - C_0] \\ &\quad \exp \left(-\frac{\mu b \Omega \ln(32 r_L/b)}{4\pi(1 - \nu) r_L kT} \right) \quad (6) \end{aligned}$$

The change in the interstitial loop radius with respect to time is given by ⁽¹⁾

$$\frac{dr_L}{dt} = -\frac{\Omega J}{2\pi b r_L} \quad (7)$$

III. GROWTH

Growth occurs during irradiation due to absorption of point defects by interstitial loops, grain boundaries, and straight dislocations. Recovery of that growth comes from the shrinkage of interstitial loops, the climb of straight dislocations by the absorption of vacancies, and by the absorption of vacancies by grain boundaries. The primary vacancy source during recovery is predicted to be the dissolution of depleted zones produced during irradiation. The strain in the basal plane caused by the interstitial dislocation loops is given by ⁽¹⁾

$$\epsilon_L = \frac{\pi}{2} b N_L r_L^2 \quad (8)$$

The strain rate in the basal plane caused by the climb of straight dislocations is given by ⁽¹⁾

$$\dot{\epsilon}_d = \frac{1}{2} \rho_0 b v_c \quad (9)$$

where

$$v_c = -\frac{2\pi D_v (C_v - C_0)}{b \ln(r_1/b)} \quad (10)$$

is the climb velocity.

The strain rate in the basal plane caused by vacancy absorption at grain boundaries is given by

$$\dot{\epsilon}_g = -\frac{k_v D_v}{\beta} [C_v - C_0] \quad (11)$$

where k_v is given by Equation (2). The total strain in the basal plane is given by

$$\epsilon_0 = \epsilon_L + \int_0^t (\dot{\epsilon}_d + \dot{\epsilon}_g) dt \quad (12)$$

The strain normal to the basal plane is given by

$$\epsilon_n = \frac{4}{3} \pi r^3 N \alpha - 2\epsilon_v \quad (13)$$

where α is the fraction of the depleted zones that are voids. The total strain in a polycrystalline specimen is assumed to be

$$\epsilon = (1 - f)\epsilon_p + f\epsilon_n \quad (14)$$

IV. RESULTS

Adamson⁽²⁾ irradiated annealed Zircaloy to fluences between 14.1 and 16.6×10^{20} n/cm² at temperatures between 216°C (420°F) and 267°C (513°F). The resultant growth was then measured. The specimens were then annealed at times between 4 and 48 hours at temperatures between 350°C (662°F) and 700°C (1292°F); at the end of the anneals the growth values were again measured. Most of the data were obtained at 417°C (783°F). Those data are shown in Figure 1. The recovery of the growth is controlled by the dissolution of the depleted zones. That dissolution is controlled to a large extent by the binding energy between a vacancy and a depleted zone. In the previous analytical work it was assumed that the binding energy was 1.1 eV. The present work indicates that better agreement between the model and the recovery data is obtained with a binding energy of 1.0 eV. The scatter in the data is about 25 percent of the total growth recovered. The theory agrees with the data within this scatter range.

Figure 2 shows predicted percent recovery versus annealing time for a material irradiated at 300°C for the fluences shown and then annealed at 427°C . Increasing the fluence greatly decreases the rate and amount of recovery. The recovery mechanism consists of the dissolution of the depleted zones and the transference of the vacancies from the depleted zones to the interstitial dislocation loops. The subsequent loop healing is responsible for the recovery of the growth. Once the depleted zones have dissolved, further healing of the dislocation loops must be by the absorption of vacancies from grain boundaries and straight dislocations. This is a much slower process. At a fluence of 10^{22} n/cm², Figure 2, the zones are dissolved after ~ 80 percent recovery of the growth.

V. ACTIVATION ENERGY OF THE RECOVERY PROCESS

Adamson's⁽²⁾ data are well suited for measuring an activation energy for the recovery process by the method developed by Howe in Reference 4. Figure 3 is a reproduction of Adamson's plot of percent of strain recovered versus annealing time for specimens annealed at 417°C and annealing temperatures for specimens annealed for 12 hours. Using the data from this plot, the apparent activation energy can be calculated by plotting the log of the annealing time at 417°C to get an equivalent amount of recovery to a similar anneal for 12 hours at a temperature whose reciprocal is plotted on the abscissa. The activa-

tion energy is proportional to the slope of the curve. Figure 4 is such a plot from the curves of Figure 3. Adamson reports an activation energy of 38 000 cal/mole as determined from the data of Figure 3 using the solid lines. From the solid line plot of Figure 4, the activation energy is found to be 41 400 cal/mole, in close agreement with Adamson⁽²⁾. However, the broken line added to Figure 3 more closely follows the data. From the broken line of Figure 3, the broken line of Figure 4 was constructed. From the broken line in Figure 4 it can be seen that as recovery proceeds the activation energy increases. The average value between 20 and 80 percent recovery is 60 800 cal/mole, considerably higher than the 41 400 cal/mole calculated from the solid line.

Also shown in Figure 3 are the theoretical predictions for both isochronal and isothermal annealing, assuming the 1.0 eV binding energy between a vacancy and a depleted zone. Using the theoretical curves of Figure 3 the predicted activation energy was calculated using the dot-dash line in Figure 4. Theory predicts 60 800 cal/mole, in agreement with the average value of the data.

In a previous work⁽³⁾ the binding energy between a vacancy and a depleted zone was given by

$$E_b \cong E_i - \frac{2\gamma\Omega}{r}, \quad (15)$$

where E_i is the vacancy formation energy, γ is the surface energy, Ω is the atomic volume, and r is the depleted zone radius. It has been found that, for in-pile growth, best results were obtained with a binding energy of 1.1 eV. In this work, post-irradiation recovery results give best agreement when the binding energy is equal to 1.0 eV. Such a decrease during a post-irradiation anneal is expected because, as the depleted zone dissolves and gets smaller, Equation (15) shows that the binding energy should decrease.

VI. CONCLUSIONS

The previously reported in-pile growth model for Zircaloy has been modified to predict post-irradiation annealing. Comparisons have been made between the theory and the growth recovery data of Adamson. It was found that by using a smaller value for the binding energy of a vacancy to a depleted zone (approximately 9 percent lower), good agreement is obtained within the limits of experimental error ± 15 percent recovered growth. The activation energy of the recovery process measured experimentally and that predicted by theory are in close agreement.

VII. ACKNOWLEDGMENTS

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Figure 1. Plot of the Percent of Growth Recovered Versus Annealing Time at 417°C Showing Comparisons Between the Data of Adamson and the Model Assuming 1.0 eV Binding Energy Between a Vacancy and a Depleted Zone

Figure 2. Plot of the Predicted Percent of Recovery Versus Annealing Time of Specimens Receiving Different Fluences

Figure 3. Plot of Isochronal and Isothermal Annealing Data of Adamson and the Theoretical Curves for Similar Conditions

Figure 4. Plot of $\ln$ Annealing Time at 417°C to get an Equivalent Recovery in 12 Hours at the Given Temperature Versus Reciprocal Temperature Used to Calculate the Apparent Activation Energies of the Recovery Process