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RESISTIVITY RECOVERY OF NEUTRON-IRRADIATED AND
COLD-WORKED THORIUM

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INTRODUCTION

Irradiation with energetic particles at low temperatures produces predominantly Frenkel defects, that is, interstitials and vacancies in equal numbers. The specific nature of the resulting microscopic radiation damage, however, depends upon a variety of factors, such as the type, energy, and dose of the incident radiation, the material being irradiated, and the temperature at which the irradiation occurs. For the same material, various irradiating particles may produce different numbers and arrangements of vacancies and interstitials in the lattice.

When metals are heated following irradiation at cryogenic temperatures, the induced point defects become mobile and may interact with one other and with extrinsic point defects. Some of the more important interactions are: annihilation of vacancies and interstitials by recombination; migration of point defects to dislocations; aggregation and trapping at impurities of point defects. In an isochronal anneal these interactions lead to the so-called recovery, in several stages, of physical properties of the samples. Each of the annealing stages is characterized by a temperature range (called the homologous temperature when expressed as a fraction of the absolute melting point), one or several activation energies of the mobile defects, depending on

whether or not the stage is subdivided and on the kinetics of interaction.

Corbett (1) and Damask and Dienes (2) have discussed several techniques for monitoring the radiation damage and for detecting various stages of the annealing process. The majority of the annealing studies conducted so far have employed electrical resistivity as a measure for the change in the defect concentration. As is well-known, the total resistivity of a metal is resolved into a residual component (ρ_0), which is independent of temperature, and another component, which is temperature dependent and associated with phonon-induced scattering of electrons. For low defect concentrations, Matthiessen's rule states that the increase in resistivity of a metal due to a small concentration of solute atoms or defects is in general independent of the temperature. Thus when the defect concentrations are sufficiently small, the increase in residual resistivity is expected to be linearly proportional to the defect or impurity concentration, since nonlinear interference effects among defects can be neglected (3).

Recovery of Irradiated Face-Centered Cubic Metals

The earliest study of postirradiation recovery by electrical resistivity measurement was conducted on face-centered

cubic (fcc) metals, notably high-purity copper. The annealing spectrum is generally divided into five major stages (4).

Stage I was first recorded in Cu below 60°K in isochronal annealing by Cooper et al. (5). Many reports (6-9) have since appeared in the literature on this stage. A characteristic of stage I is the subdivision into five substages. Corbett et al. (8,9) attributed the substages I_A , I_B , and I_C to the recombination of close Frenkel pairs, I_D to recombination of interstitials with their own vacancies in a small number of jumps (correlated recombination), and I_E to recombination involving other vacancies in a large number of jumps (uncorrelated recombination). Recent studies (10,11) using field-ion microscopy (FIM) have substantiated the annealing mechanism of stage I, which involves migration of free interstitials.

Stage II occurs in the temperature range between the termination of free interstitial migration in stage I and the beginning of migration of a second type of defects in stage III. The onset of this stage depends sensitively on the purity of the sample, the irradiation dose, and the type of bombarding particles. Experimental results (12-19) obtained from dilute alloys of Al or Cu indicate that the presence of impurity atoms gives rise to subdivision of stage II as in stage I. Despite these results, stage II has not been systematically studied because of the rather complex

behavior of the irradiation-induced defects and the sensitive dependence on impurities. Thus the recovery processes responsible for stage II are not well understood. The conceivable interpretation of stage II recovery is based on the detrapping of interstitials from impurity atoms or on the rearrangement or coagulation of the interstitial clusters formed in stage I (12,13,21,22).

Stage III recovery occurs in Cu, Ag, Ni, Al, and Pt at about 0.2 to 0.25 T_m . After electron irradiation, recovery in this stage shows a dose dependence in Al (16,23), Cu (24), Au (25,26), and Pt (27). In all these metals a single well defined peak has been observed in stage III, which is, however, shifted to lower temperatures with increasing irradiation dose. A subdivision of stage III has been observed in Al irradiated by fast neutrons. Substages have also been observed in Cu, Au, and Ag at low neutron doses (22,28). An increase in dose tends to shift the high temperature peaks to lower temperatures until the subpeaks converge.

The origin of stage III has been a subject of controversy for some time. Both vacancy and split-interstitial migrations have been proposed (21) for fcc metals. For bcc metals an extrinsic process, which involves the migration of interstitial impurity atoms, has been proposed in addition to the intrinsic process. Considerable evidence has been accumulated to support the migration of interstitial impurity

atoms in group VA metals (V, Nb, and Ta) and α -Fe (29,30,31, 32). For the identification of stage III mechanisms, a reliable determination of activation energy for migration of the involved defects is of extreme importance.

The influence of such impurity atoms as Mg, Zn, Cu, Ag, and Sn on stage III recovery in neutron and electron irradiated Al has been studied most extensively by Dimitrov-Frois et al. (33-37), Peters and Shearin (16), and Sosin et al. (17, 38). The activation energies deduced for the dilute alloys of Al seem to be the same as that observed in pure Al. For fcc metals other than Al, little information is available about the influence of impurities on stage III recovery.

Recovery of Cold-Worked

Face-Centered Cubic Metals

Plastic deformation is expected to produce dislocations and point defects of both vacancy and interstitial type. The recovery stages of deformed metals are related largely to the annealing of point defects (39). The recovery of cold-worked fcc metals has been reviewed by Balluffi et al. (40) and van den Beukel (41). Isochronal recovery on Al, Au, Pt, Ni, Ag, and Cu after heavy plastic deformation at 78°K (at 20°K for Al) features two main stages (II and III, or III and IV for Pt for no good reason) (42-46).

Stage II recovery has not been investigated as extensively as stage III. In Cu, Ni, and Ag, stage II shows

substages and shoulders, whereas in Al, Au, and Pt it features well-defined peaks. It was shown by Buck (47) that stage II recovery in heavily cold worked Cu single crystals is about the same in 99.98 and 99.999% pure samples, indicating that stage II is probably intrinsic rather than extrinsic. Stage II recovery has been interpreted by several workers (48-53). While van den Beukel (41) explained stage II in terms of migration or break up of interstitial agglomerates, Corbett (48) suggested that stage II recovery is due to the release of interstitials previously trapped by impurities.

All cold worked fcc metals show pronounced stage III recovery. In some metals such as Cu, Ni, and Al, stage III involves several substages, whereas in others (Au and Pt), no substages are observed. The relationship between the fine structure of stage III and the degree of deformation is not clearly known.

It is difficult to devise critical experiments to identify the point defects involved in stages II and III in cold-worked metals. The interpretation of the recovery spectrum of cold-worked metals requires pertinent data obtained from other studies, such as equilibrium, quenching, and irradiation experiments. With the possible exception of Ag, Ni, and Au, the activation energies deduced for the irradiated fcc metals such as Pt, Al, and Cu agree reasonably

well with those deduced from deformation experiments (41). Stage III of irradiated or cold-worked Pt and Al is commonly attributed to the migration of single vacancies (16, 38, 42, 54). For Ag, Ni, and Au there is some doubt as to whether stage III involves the same process for cold-worked and irradiated samples because of the somewhat higher activation energies deduced for the irradiated samples. Seeger *et al.* (55, 56) have thus proposed that for the case of irradiation, stage I is due to the migration of free interstitials of the $\langle 110 \rangle$ crowdion form and stage III involves the migration of interstitials of the $\langle 100 \rangle$ split or dumbbell configuration. Data for stage III recovery of cold-worked fcc metals seem to support either the single vacancy or a di-vacancy migration model (41, 57-59).

Recovery Studies of Irradiated Thorium

Considerable interest has been generated in Th by virtue of the potential application of the metal as a breeder of the fissionable ^{233}U via chain reactions. However, resistivity recovery study of low temperature (80°K or below) deformed Th is still not available and there have been only three studies in which resistivities of irradiated thorium have been measured. Brinkman and Gilbert (60) observed a saturation effect in the resistivity of Th after bombardment by 9 MeV protons. Subsequent irradiation with

18 MeV deuteron bombardment was found to produce a reduction in the saturation value of the resistivity.

Bowman et al. (61) measured the electrical resistivity of a 0.17 mm Th foil at -146°C after irradiation by 19 MeV deuterons at -70°C for various periods and annealing at temperatures up to 100°C . The resistivity showed a saturation effect analogous to that observed by Brinkman and Gilbert. Exposure of Th to 38 MeV alpha particles also caused a saturation effect, which was incomplete, however, due to insufficient irradiation. Isochronal anneal for one hour at $200-300^{\circ}\text{C}$ was shown to bring about a complete recovery of the damage.

More recently, Schmidt (62) introduced radiation damage in 99.9% pure Th by homogeneously doping the metal with a short-lived isotope (^{228}Th) at 4.2°K . Subsequently an isochronal anneal was conducted between 4.2 and 1150°K . This annealing range covers stage I through IV as shown in Figure 1. The various stages occurred approximately at $4.2-48^{\circ}\text{K}$ for stage I, $48-230^{\circ}\text{K}$ for stage II, $230-400^{\circ}\text{K}$ for stage III, and $400-1100^{\circ}\text{K}$ for stage IV. Stage I was studied in greater detail than other stages. Five substages were found in stage I in analogy to Cu except that the substage peaks were not so well-defined in Th. Activation energies determined for the stages below 80°K were: $I_B - 0.021 \pm 0.002$ eV, $I_D - 0.0875 \pm 0.002$ eV, $I_E - 0.0869 \pm 0.002$ eV, $II_A - 0.100 \pm 0.01$ eV and $II_B - 0.182 \pm 0.01$ eV.

Figure 1. Isochronal recovery curve for thorium damaged by internal alpha decay at 4.2°K. Resistivity measured at 4.2°K following 15-min. anneals at the temperatures indicated (69).

Several reports have revealed pronounced influences of carbon on the mechanical properties of Th (63, 64), notably (1) the emergence of a yield point whose magnitude increases with the C content; (2) a strain-rate sensitivity; (3) a ductile-brittle transition temperature when the C content exceeds 500 wt ppm; (4) impurity strengthening; and (5) a relatively strong temperature dependence of the flow stress. All these effects are normally associated with bcc metals and very atypical of the fcc metals. Zerwekh and Scott (65) and Peterson et al. (63, 64) have thus concluded that the carbon atoms in thorium must interact strongly with dislocations, thereby controlling the deformation behavior below room temperature according to Friedel's random solute barrier mechanism (66). The reason for the unusually strong interactions of C atoms with dislocations in Th is not known, however.

As mentioned previously, there are two possible interpretations for the stage III recovery of fcc metals -- the migration of vacancies and the migration of interstitials of the $\langle 100 \rangle$ dumbbell form. In bcc metals such as α -Fe, V, Nb, and Ta, stage III is explained in terms of interstitial impurities migration. The unusual mechanical behavior of Th metal containing C described has generated considerable interest in regard to the effect of C on the recovery behavior of Th deformed or irradiated at cryogenic

temperatures. The present study was initiated with the hope that a better understanding could be attained of the annealing processes in stages II and III and of the role played by C atoms in these processes.

Electrical resistivity measurements were chosen as the means to measure the change in defect concentration. This approach has the advantage of high sensitivity and accuracy and is easy to perform. Although it is difficult to specify the type of defects responsible for resistivity change, valuable information has been gained from the measurements concerning the dependence of the resistivity recovery on the initial defect density, which, in turn, varies with the fluence of fast neutrons or with the degree of deformation and with impurities.

EXPERIMENTAL PROCEDURE

Specimen Preparation

Pure thorium and thorium-carbon alloys were prepared by electron-beam melting. The starting materials were arc-melted into fingers (67) and drawn into wire. An intermediate annealing was performed before the wires reached their final diameter of about 0.70 mm with a length of about 40 mm. The final anneal was done in vacuum (residual pressure $\sim 2 \times 10^{-7}$ torr) at 800°C for four hours. Before and after each anneal, specimens were thoroughly cleaned in a mixture of one part water, one part concentrated nitric acid and a small amount of sodium silicofluoride (Na_2SiF_6). All specimens were stored in an evacuated desiccator to avoid oxidation.

For an accurate determination of the state of purity of the final annealed and cleaned specimens, a complete chemical analysis was performed involving various techniques. Notably the wet process for carbon spectrography for metallic impurities, and vacuum fusion for gaseous (oxygen, nitrogen, and hydrogen) impurities. The results of the chemical analysis are shown in Table 1.

Irradiation Experiments

Neutron irradiation experiments were conducted in a cryostat installed in the V-2 thimble of the Ames Laboratory

Table 1. Analysis of annealed thorium specimens in ppm by weight

Specimen	C	O	H	N	Al	Be	Ca	Cr	Fe	Mg	Mn	Ni	Si	Zr
T-59	30	150	10	35	~30	<20	<25	~40	<20	<20	<20	<50	<20	<100
T-1	45	160	7	20	~50	~100	<20	<u><20</u>	~40	<20	<20	<20	<20	<200
TC512	300	180	1	17	~30	<20	<25	~50	<20	<20	<20	<50	<20	<100
TC52a	600	180	9	15	~30	<20	<25	<u><20</u>	<20	<20	<20	<50	<20	<100

Research Reactor. The cryostat was installed inside a flux converter which had a cadmium shield of 0.78 mm thickness. The fast neutron flux was about 1.5×10^{12} n/cm²-sec ($E > 0.1$ MeV). The specimens were immersed in liquid nitrogen and temperature was recorded by two copper-constantan thermocouples attached to the specimen tube. Irradiation was conducted with fluences at 1.3×10^{18} n/cm² ($E > 0.1$ MeV). After irradiation, the specimens were transferred to a liquid nitrogen dewar for storage and for decay of induced radioactivity. Care was exercised to avoid a temperature rise during the transfers from the Reactor to the storage dewar and from the dewar to the specimen holder.

Cold-Work Experiments

Samples were deformed by compression in liquid nitrogen by amounts ranging from about 5 to 40%. The apparatus used for low-temperature compression was similar to that described by Dimitrov and Dimitrov-Fois (68). The wire was compressed between the plane surfaces of two heat-treated steel disks, immersed in liquid nitrogen. The deformed specimens were mounted on the specimen holder, which had been constructed for resistivity measurements at 80°K and annealing.

For square wires of side e_0 , the amount of deformation corresponding to a final thickness e would be $\bar{\epsilon} = \ln e_0/e$.

However, this formula cannot be used for wire which has initially a circular cross-section. The following relationship was established (68):

$$\bar{\epsilon} = \ln \frac{e_0}{e} - \frac{1}{2} \left[1 - \left(\frac{e}{e_0} \right)^2 \right] \quad (1)$$

by assuming that the cross-section of the compressed wire can be approximated by a rectangle plus two half-circles.

Annealing Experiments

Both isochronal and isothermal annealing of irradiated or deformed specimens from 120 to 400°K were carried out in a constant temperature bath, using three different baths:

- (1) Freon 12 precooled by liquid nitrogen for 120 to 200°K;
- (2) absolute ethyl alcohol precooled by liquid nitrogen and Freon 12 and heated by a resistance winding with a Bayley precision temperature controller for 220 to 320°K; and (3) Dow Corning 550 fluid with the same heater and temperature controller for higher temperatures. The temperature of the annealing bath can be controlled and maintained to within $\pm 0.5^\circ\text{K}$.

Electrical Resistivity Measurement

Electrical resistivity was measured by the standard four-probe dc potentiometric technique. A Rubicon (model 2768) six-dial potentiometer was used, which has a sensitivity of $\pm 0.01 \mu\text{v}$. To support the high precision

emf measurements by the Rubicon potentiometer, the input current (~ 0.5 A) was stabilized by a North-Hills precision constant current source, which control the current within ± 1 μ A. The current source was calibrated with respect to a Leeds-Northrup standard resistor. A normal-and-reverse procedure is used to compensate the effect caused by spurious thermal emfs in the circuit. The measurements were made on specimens immersed in liquid nitrogen at one atmosphere pressure. Absolute resistivity values were estimated to be accurate to $\pm 1\%$, primarily from errors in measuring the specimen cross-section and the length between the potential leads. Relative errors were less than ± 0.0001 $\mu\Omega$ -cm, however.

RESULTS

Isochronal Annealing

The recovery of the neutron irradiation-induced resistivity for the specimens irradiated to 1.3×10^{18} n/cm² ($E > 0.1$ MeV) is shown in Figure 2. Here the percentages of recovery are plotted against the temperatures at which the specimens underwent 15-minute anneals. The differential curves which show the peaks in different stages are also shown in the same figure. For better precision, two specimens of each composition were examined. The annealing was conducted from 120°K up to 420°K, and two stages can be seen from the recovery spectra. Following Schmidt's (62) designation, the main recovery stage is named stage III, which covers the temperature range from about 240 to 400°K for both pure Th and Th-C alloys. The excess resistivities induced by irradiation are designated as $\Delta\rho_0$, which is seen to be larger in the Th-C alloy. However, the percentage of recovery at the end of stage III is higher in pure Th. The differential recovery spectra show the main peak position at about 320°K (0.16 T_m) for both pure Th and the Th-0.03 w/o C alloy. It will be shown that the addition of carbon atoms to thorium seems to enhance stage II recovery and to suppress stage III recovery.

Figure 3 shows the recovery of resistivity in three specimens of pure Th induced by cold-work of different

Figure 2. Isochronal recovery and differential recovery curves for pure Th (T-59) and Th-0.03 w/o C alloy (TC512) irradiated at 80°K. Resistivity measured at 80°K following 15-min. anneals at the temperatures indicated (10°K interval). ρ_I is the as-irradiated resistivity, ρ_u the residual resistivity, and $\Delta\rho_0 = \rho_I - \rho_u$ is the resistivity increase by irradiation.

Figure 3. Isochronal recovery and differential recovery curves for pure Th deformed at 80°K. Resistivity measured at 80°K following 15-min. anneals at the temperatures indicated (10°K interval). $\Delta\rho_0$ is the resistivity increase by deformation.

amounts at 80°K. The recovery spectra are seen to be clearly divided in two main parts in all cases. The two main recovery ranges are conventionally called stage II and III (41). The temperature ranges for stages II and III recovery peaks are about from 150° to 240°K and 240° to 400°K, respectively. These ranges are seen to be independent of the amount of deformation. Stage III temperature range corresponds to the main recovery stage in the irradiated specimens described previously. Figure 3 shows a shift of the peak temperatures of stage III for pure Th from 333 to 318°K with deformation increasing from 17% to 36%. This trend is also observed in the Th-C alloys in Figures 4 and 5. Also, in the latter figures a slight increase of stage III peak intensity with increasing deformation is observed; whereas in Figure 3 for pure Th an increase in deformation does not seem to change the stage III peak intensity. The peak position for stage II is seen to be independent of deformation from Figures 3-5, while the peak intensity for stage II slightly increases with increasing deformation for both pure Th and the Th-C alloys.

The addition of carbon to Th causes a small shift of the stage II peak position. As shown in Figure 6, for instance, the peak temperature of stage II is lowered from 203°K to 196°K as a result of adding 0.06 w/o C to Th. The most noticeable effect on the recovery spectrum of adding carbon atoms to Th is, however, the suppression of peak height at

Figure 4. Isochronal recovery and differential recovery curves for Th-0.03 w/o C alloy deformed at 80°K. Resistivity measured at 80°K following 15-min. anneals at the temperatures indicated (10°K interval). $\Delta\rho_0$ is the resistivity increase by deformation.

Figure 5. Isochronal recovery and differential recovery curves for Th-0.06 w/o C alloy deformed at 80°K. Resistivity measured at 80°K following 15-min. anneals at the temperatures indicated (10°K interval). $\Delta\rho_0$ is the resistivity increase by deformation.

Figure 6. Dependence of isochronal recovery and differential recovery curves on carbon content for Th deformed to 17% at 80°K. Resistivity measured at 80°K following 15-min. anneals at the temperatures indicated (10°K interval).

$\sim 200^\circ\text{K}$, although the total percentage of recovery in stage II is almost unchanged. Figure 6 shows that the recovery curves become more flatter and smooth with increasing carbon content. The temperature range for stage III is observed to be from 250 to 400°K which has very little effect due to either increase of deformation or carbon content. Finally, Figure 6 reveals that the influence of carbon on the peak intensity of stage III recovery is negligibly small, although the peak temperature lowered from 333°K to 313°K as a result of adding 0.06 w/o C to thorium.

Activation Energies

The activation energy, E , for a recovery stage or sub-stage is determined by a comparison of the recovery rates, $d\Delta\rho/dt$, measured at different temperature, T , for identical values of a temperature-independent function, G , based on the equation (22):

$$-\frac{d(\Delta\rho)}{dt} = G(\Delta\rho, \{0\}) K_0 \exp(-E/kT) \quad (2)$$

where $\Delta\rho$ is the measured resistivity change, K_0 , a constant, and k the Boltzmann constant. The factor G has identical values at different temperatures only if $\Delta\rho$ and the initial damage state symbolized by $\{0\}$ are identical. From this requirement, E is deduced by measuring the change of annealing temperature from T_1 to T_2 . The activation energy is thus

given by

$$E = \frac{kT_1T_2}{T_2-T_1} \ln \left[\left(\frac{d\Delta\rho}{dt} \right)_{T=T_2} / \left(\frac{d\Delta\rho}{dt} \right)_{T=T_1} \right] \quad (3)$$

where $\left(\frac{d\Delta\rho}{dt} \right)_T$ is the slope of the isothermal curve at temperature T , which can be evaluated in the $\Delta\rho$ or ρ versus t plot. In practice, it is somewhat difficult to construct an accurate slope, and therefore more than one experiment is usually performed. This so-called "ratio-of-slope method" has the important advantage that the requirement of identical defect configurations at the two temperatures studied is fulfilled automatically. The results of applying the ratio-of-slope method to the recovery data for irradiated specimens are shown in Figures 7 and 8 for the Th-0.03 w/o C alloy. The average activation energies obtained for stages II and III recovery in the Th-C alloy are 0.55 and 1.07 eV, respectively. For irradiated pure Th the average activation energy for stage III recovery was also determined by the ratio-of-slope method, which yields $E_{III} \approx 1.14$ eV. No value has been obtained in the stage II range.

The activation energies of stage II and stage III recovery in cold-worked specimens have been determined exclusively by use of the ratio-of-slope method. Typical examples for determining the activation energy in stage II for deformed Th, Th-0.03 w/o C, and Th-0.06 w/o C alloys are shown in Figures 9, 10, and 12, respectively. The deduced

Figure 7. Determination of activation energy of stage II by the ratio-or-slope method for Th-C alloy irradiated at 80°K. Resistivity measured at 80°K.

Figure 8. Determination of activation energy of stage III recovery by the ratio-of-slope method for Th-C alloy irradiated at 80°K. Resistivity measured at 80°K.

Figure 9. Determination of activation energy of stage II recovery by the ratio-of-slope method for pure Th deformed at 80°K. Resistivity measured at 80°K.

Figure 10. Determination of activation energy of stage II recovery by the ratio-of-slope method for Th-0.03 w/o C alloy deformed to 21% at 80°K. Resistivity measured at 80°K.

Figure 11. Determination of activation energy of stage II recovery by the ratio-of-slope method for Th-0.03 w/o C alloy deformed to 8% at 80°K. Resistivity measured at 80°K.

Figure 12. Determination of activation energy of stage II recovery by the ratio-of-slope method for Th-0.06 w/o C alloy deformed at 80°K. Resistivity measured at 80°K.

values thus obtained for E_{II} from experimental data are listed in Table 2. The experimental error involved in deducing the activation energies is estimated to be approximately 6%, which is about the same as the mean deviation from the average value of E . In Table 3 only the experimental scatters are shown, which reflect the reproducibility of the measurement. As the carbon content is increased, the E_{II} value tends to decrease slightly. This tendency is also seen in Figures 9, 10, and 12. The dependence of activation energy on deformation, however, is not so obvious. Some examples are shown in Figures 10 and 11. Although the deformation has been increased from 8 to 21%, the change in energy is still only 0.03 eV, which is within the uncertainty range.

Figures 13-15 show the determination of activation energy of stage III recovery, E_{III} , for deformed specimens of Th and ThC alloys by use of the ratio-of-slope method. The results are listed in Table 2. The average values of E_{III} are 1.16 ± 0.08 , 1.10 ± 0.10 , and 1.08 ± 0.08 eV for pure Th, 0.03 w/o C, and 0.06 w/o C alloys, respectively. As in stage II, the stage III activation energy also decreases slightly as the carbon content is increased; otherwise, it is rather independent of deformation.

An alternate method for determining E is the Meehan-Brinkman (MB) method. If equation (2) is integrated,

$$\int_{\Delta\rho_1}^{\Delta\rho_2} - \frac{d(\Delta\rho)}{G(\Delta\rho, \{0\})} = \left(\int_{t_1}^{t_2} dt \right) K_0 \exp(-E/kT) \quad (4)$$

Table 2. Average activation energy obtained by ratio-of-slope method in deformed thorium

Stage II			Stage III		
Specimen (number)	$\bar{E}_{II}$ (eV)	Deformation (%)	Specimen (number)	$\bar{E}_{III}$ (eV)	Deformation (%)
T-1 (12-1)	0.57 ± 0.07	33	T-1 (8-3)	1.19	17
T-1 (12-2)	0.59 ± 0.07	30	T-1 (12-1)	1.12	33
T-1 (12-3)	0.67 ± 0.01	39	T-1 (12-2)	1.10 ± 0.01	30
T-1 (158)	0.62 ± 0.04	41	T-1 (168)	1.27	13
			T-1 (142)	1.27	27
Total Ave: $\bar{E}_{II} = 0.61 \pm 0.07$			$\bar{E}_{III} = 1.16 \pm 0.08$		
TC512 (27-1)	0.56 ± 0.06	21	TC512 (27-1)	1.12 ± 0.03	21
TC512 (27-5)	0.56 ± 0.07	8	TC512 (27-7)	1.08 ± 0.10	21
TC512 (27-7)	0.59 ± 0.02	21			
TC512 (166)	0.59 ± 0.05	13			
TC512 (158)	0.59 ± 0.03	7			
Total Ave: $\bar{E}_{II} = 0.57 \pm 0.07$			$\bar{E}_{III} = 1.10 \pm 0.10$		
TC52a (18-1)	0.55 ± 0.03	28	TC52a (12-1)	1.08	15
TC52a (18-2)	0.56 ± 0.01	22	TC52a (18-1)	1.12 ± 0.04	28
			TC52a (142)	1.03 ± 0.10	19
Total Ave: $\bar{E}_{II} = 0.55 \pm 0.07$			$\bar{E}_{III} = 1.08 \pm 0.08$

Figure 13. Determination of activation energy of stage III recovery by the ratio-of-slope method for pure Th deformed at 80°K. Resistivity measured at 80°K.

Figure 14. Determination of activation energy of stage III recovery by the ratio-of-slope method for Th-0.03 w/o C alloy deformed at 80°K. Resistivity measured at 80°K.

Figure 15. Determination of activation energy of stage III recovery by the ratio-of-slope method for Th-0.06 w/o C alloy deformed at 80°K. Resistivity measured at 80°K.

The lefthand side of equation (4) is a pure number because the integral between the values of two fixed limits is a constant. Thus, we obtain an expression

$$\Delta t \exp(-E/kT) = \text{constant} \quad (5)$$

where Δt is the time interval between the two Δp values. Utilizing equation (5) it is possible to superimpose the isochronal and isothermal recovery curves provided that the two specimens have the same initial damage stage. Under this condition, we further have

$$\Delta t_c \exp(-E/kT_c) = \Delta t_i \exp(-E/kT_i) \quad (6)$$

where the subscripts c and i denote the isochronal and isothermal annealing processes, respectively. For the isothermal process, T_i is a constant; and for the isochronal process, Δt_c is a constant. Hence the following equation can be deduced from equation (6)

$$\ln \Delta t_i = \text{constant} - E/kT_c. \quad (7)$$

Based on equation (7), a graph of $\ln \Delta t_i$ vs $1/T_c$ should display a straight line with the slope being equal to $-E/k$.

The results of applying the MB method for determining the stage III activation energy to the recovery data obtained from irradiated specimens are shown in Figures 16-18. The average activation energies obtained from the MB method for pure Th and the w/o C-Th alloy are 0.98 ± 0.01 and 0.95 ± 0.03 eV, respectively.

A third method known as the cross-cut method is based on equation (2) by using two or more isothermal annealing curves

Figure 16. Determination of activation energy of stage III recovery by the MB method for pure Th irradiated at 80°K to a fluence of 1.3×10^{18} n/cm² ($E > 0.1$ MeV). T_i , T_c , and Δt_i are as defined in equation (6).

Figure 17. Determination of activation energy of stage III recovery by the MB method for Th-0.03 w/o C alloy irradiated at 80°K to 1.3×10^{18} m/cm² ($E > 0.1$ MeV). The isothermal annealing temperature is 320°K.

Figure 18. Determination of activation energy of stage III recovery by the MB method for Th-0.03 w/o C alloy irradiated at 80°K to 1.3×10^{18} n/cm² (E > 0.1 MeV). The isothermal annealing temperature is 310°K.

on a set of identical specimens, i.e., specimens containing the same initial concentration of defects. In this case, equation (5) can be rewritten as:

$$t_1 \exp[-E/kT_1] = \text{constant} \equiv C, \quad (8)$$

where t_1 is the time required to reach a constant value of $\Delta\rho$ at annealing temperature T_1 . When the cut crosses several curves, the times given by the intersecting points are related to the pertinent temperatures by

$$\ln(t_1) = \ln C + E/kT_1. \quad (9)$$

Equation (9) enables E to be evaluated from the slope of a straight line fitting the data points in the plot of $\log t_1$ against $1/T_1$. If a cut is taken at another ordinate point in the $\Delta\rho$ vs t_1 plot, only the constant C is altered in equation (9) and the lines described by this equation should be parallel if the process features a single activation energy. The results of applying this method for determining the stage III activation energy in the irradiated Th-C specimens are shown in Figure 19. By using a least-square fit, the activation energy is estimated. The two straight lines in Figure 19 are not exactly parallel. The deduced activation energy, E , are 1.01 and 0.94 eV, which are close to the values deduced from other methods.

A comparison of all deduced average values for E from the three methods is given in Table 3, which indicates that,

Figure 19. Determination of activation energy of stage III recovery by the cross-cut method for Th-0.03 w/o C alloy irradiated at 80°K to 1.3×10^{18} n/cm² ($E > 0.1$ MeV). T_i and t_i are as defined in equation (8). f is the normalized resistivity value.

Table 3. Average activation energy for stage III recovery in neutron-irradiation thorium

Pure Th (T-1)			Th-0.03 w/o C (TC512)		
Method	Number of independent specimens	Average activation energy, $\bar{E}_{III}$ (eV)	Method	Number of independent specimens	Average activation energy, $\bar{E}_{III}$ (eV)
Ratio-of-slope	1	1.14 ± 0.04	Ratio-of-slope	2	1.07 ± 0.06
Meechan-Brinkman	2	0.98 ± 0.01	Meechan-Brinkman	4	0.95 ± 0.03
			Cross-cut ^a	3	0.98 ± 0.04

^aActivation energies obtained by the method of cross-cut vary with the normalized resistivity, f . They increase from 0.78 to 1.07 eV as f values change from 0.6 to 0.2. Due to the scattering of data points, this value was not obtained for pure thorium.

Figure 20. Isothermal annealing curves of stage III for pure Th and Th-0.03 w/o C alloy irradiated at 80°K to 1.3×10^{18} n/cm² (E > 0.1 MeV). The annealing temperature is 335°K.

Figure 21. Isothermal annealing curves of stage III for pure Th and Th-0.03 w/o C alloy irradiated at 80°K to 1.3×10^{18} n/cm² ($E > 0.1$ MeV). The annealing temperature is 320°K.

Figure 22. Isothermal annealing curves of stage III for pure Th and Th-0.03 w/o C alloy irradiated at 80°K to $1.3 \times 10^{18} \text{ n/cm}^2$ ($E > 0.1 \text{ MeV}$). The annealing temperature is 310°K .

Figure 23. Log-log plots of $\ln 1/f$ versus annealing time for irradiated specimens annealed at different temperatures. The curves are shifted along the ordinate relative to each other for clarity.

the values deduced by the MB method are somewhat lower than values deduced by the ratio-of-slope method.

Isothermal Annealing and Kinetics

For the purpose of analyzing the annealing kinetics and obtaining activation energies by the MB and cross-cut methods, irradiated Th and the Th-C alloy were annealed isothermally in three different temperatures close to the stage III peak position, 320°K. Figures 20, 21, and 22 show the results of isothermal annealing for Th and the 0.03 w/o C-Th alloy at 335°, 320°, and 310°K, respectively. In these figures, the normalized resistivity or the fractional resistivity remained in stage III, $f = \frac{\Delta\rho}{\Delta\rho_0} = \frac{\rho - \rho_\infty}{\rho_0 - \rho_\infty}$, is plotted against the annealing time, where ρ is the measured resistivity at time t , ρ_0 the resistivity at the beginning of stage III recovery, ρ_∞ the resistivity at the end of stage III. Values for ρ_0 and ρ_∞ were determined from the isochronal recovery curves. The smooth curves in Figures 20-22 were calculated from the Avrami empirical equation (69),

$$f = \exp[-(\alpha t)^n], \quad (10)$$

where α and n are constants independent of f (and thus of t) at constant temperature. To determine n and α , the factor $\log[-\ln f]$ was plotted against $\log t$, as shown in Figure 23. The deduced values for the exponent n are

0.28 - 0.31, 0.32 - 0.35, and 0.43 for annealing at 310, 320, and 335°K, respectively, showing a slight increase with increasing temperature, but an independence on the carbon content. Combining Figures 20-22, Figures 24 and 25 reveal the temperature effect on the isothermal annealing in pure Th and the 0.03 w/o C-Th alloy. The curves for pure Th do not fit the data points very well at the beginning of the anneal; the fitting was satisfactory thereafter.

Isothermal anneals at 335°K were also performed for cold-worked Th-0.03 w/o C alloy to different strains. The results are shown in Figure 26, where the normalized resistivity at 78°K, f , is plotted against annealing time. A good fit to the empirical equation $f = \exp[-(at)^n]$ was obtained. Values for the exponent n were determined by plotting $\log(-\ln f)$ against $\log t$ in Figure 27. The deduced values for n are 0.55 and 0.60 for deformed Th-0.03 w/o C alloy deformed to 13% and 5%, respectively.

Figure 24. Isothermal annealing curves for irradiated pure Th specimens at different temperatures.

Figure 25. Isothermal annealing curves for irradiated Th-0.03 w/o C alloy specimens at different temperatures.

Figure 26. Isothermal annealing curves for cold-worked Th-C alloy specimens at 335°K.

Figure 27. Log-log plots of $\ln 1/f$ versus annealing time for cold-worked Th-C alloy specimens annealed at 335°K.

DISCUSSION

Nature and Extent of Radiation Effect on the
Resistivity of Thorium at 80°K

The excess resistivities, $\Delta\rho_0$, induced in thorium specimens by cold work or irradiation at 80°K are compared in Table 4. For the same fluence, the $\Delta\rho_0$ value is seen to increase with increasing carbon content. This carbon effect is similar to that reported on neutron-irradiated specimens of the Al-Ge (0.02 - 0.5 at %) alloys by Kontolen et al. (70). The dependence of $\Delta\rho_0$ on carbon content is also detected in cold worked specimens. To interpret the carbon

Table 4. Comparison of excess resistivity values for thorium specimens after deformation and irradiation at 80°K

	Cold work		Neutron irradiation	
	$\Delta\rho_0$ ($\mu\Omega$ -cm)	Deformation	$\Delta\rho_0$ ($\mu\Omega$ -cm)	Fluence (n/cm^2)
T-59	0.47	17%	1.10	1.3×10^{18} ($E > 0.1$ MeV)
Tc512	1.30	17%	1.38	1.3×10^{18} ($E > 0.1$ MeV)
Tc512	1.48	21%		
Tc52a	1.60	17%		

effect on $\Delta\rho_0$, let us first refer to the work by Schmidt (62), who examined the resistivity recovery between 4.2° and 80°K from radiation damage by internal alpha decay in thorium at 4.2°K. He has concluded that migration of free interstitials is responsible for stage-I_E at 35°K and that stage II has two substages, II_A and II_B, centering around 55° and 73°K. Following his conclusions, we assume that free interstitials would move very rapidly at 80°K. As described by Horak and Blewitt (71), irradiation with fast neutrons at 4.2°K will primarily generate damage zones composed of vacancies, interstitials, and their clusters. At 80°K, the interstitials induced inside the zones will either recombine with vacancies, conglomerate into clusters of variable sizes, or be trapped by impurities. After the irradiation at 80°K, relatively few free interstitials can survive. The radiation-induced resistivity increment is then composed of contributions caused by vacancies, trapped interstitials, and clusters of both interstitials and vacancies.

It has been suggested (72) that traps or sinks for interstitials (and vacancies) may be termed unsaturable, saturable, and nucleational. This classification of traps is based on whether or not the capture radius of the trap would vary with defects already trapped. For unsaturable traps (dislocation, grain boundary, etc.), the capture

radius is independent of the number of interstitials captured, whereas for saturable traps (vacancies and their clusters) the capture radius decreases with increasing number of "trapped" interstitials. The capture radius of nucleational traps (both homogeneous and heterogeneous nuclei), on the other hand, increases with increasing number of trapped interstitials. In this classification, if impurity atoms act as nucleational traps for interstitials, the "concentration" of trapping sites (concentration of impurity atoms times capture volume of that impurity atom), as suggested by Wollenberger (72), would increase with increasing impurity content. On the other hand, under the same fluence of irradiation, the "concentration" of recombination sites (vacancy concentration times capture volume of vacancies) would have a constant value. If all specimens had the same thermal history before irradiation, the "concentration" of unsaturable sink sites (concentration of traps times capture volume per trap) in all specimens should also have a constant value. Hence, the probability that the migrating interstitials would recombine would be increased with increasing purity or decreasing impurity content. This reasoning has been shown mathematically and experimentally by Dworschak et al. (73) for electron-irradiated copper. The present observation that for a given neutron fluence, the excess resistivity values for the

Th-0.03 w/o C alloy specimens are higher than those for pure Th is what should be expected according to this trapping mechanism.

Peterson and Skaggs (63) observed that flow stress of thorium increased with increasing carbon content and the increase is much greater when deformation is performed at lower temperatures. They assumed that this strengthening effect is due to a strong interaction between moving dislocations and carbon atoms. In their interpretation, carbon atoms were assumed to act as strong obstacles to moving dislocations. Using a bond-energy model, they proposed that the lattice strain of a dislocation near a carbon atom in solution would be such as to change the length and orientation of the thorium-carbon bonds and therefore the bond energy. This change of energy implies in a strong dislocation-carbon atom interaction. For stronger interactions, the yield stress is increased and the dislocation bows to a smaller radius of curvature. After the dislocation passes through the carbon atoms, small dislocation loops would be generated around the carbon atoms. These loops can then interact with other dislocations and produce point defects by Friedel's model (41). Hence, it is possible that both the concentrations of the generated point defects and in dislocation density increase with increasing carbon content under the

same amount of deformation. The increase in excess resistivities of the Th-C alloys shown in Table 4 may serve to justify this reasoning.

Interpretation of Stage II Recovery above 80°K

Dworshak et al. (74) have recently investigated the interaction of migrating interstitials with substitutional impurities in dilute copper alloys irradiated with electrons between 50° and 170°K. By applying the pertinent diffusion theory of self-interstitials, the capture radii of various impurities for migrating interstitials and the resistivity induced by trapped interstitials have been determined. The deduced capture radii of all impurities (Au, Ge, Ni, Pd, Sb, and Zn) studied except Be were found to decrease with increasing irradiation temperature and become zero at about 110°K. From the coincidence of this temperature with the stage II temperature range for copper, they concluded that stage II recovery for copper is caused by the detrapping of interstitials.

Although the change in capture radius of carbon atoms for migrating interstitials in thorium with temperature is still unknown, the enhancement of stage II_C recovery observed in the irradiated Th-0.02 w/o C specimens suggests that detrapping of interstitials from impurities might be

the dominant mechanism for the stage II_C recovery. The detrapped interstitials may then migrate (1) to form clusters, (2) to recombine with vacancies, and (3) to other stronger traps.

In deformed thorium the number of dislocations present is so large that they act as the primary sinks. Generally, for a dislocation network the average number of jumps of a point defect to reach a dislocation in random walk is of the order (41),

$$n_j \approx \frac{1}{\Lambda a^2} \approx \frac{10^{15} (\text{cm}^{-2})}{\Lambda} \quad (11)$$

where Λ is the dislocation density and a the interatomic distance. (The number of jumps is smaller when the diffusion is assisted by the dislocation stress fields and larger when the dislocation distribution is nonuniform.) Another consequence of high density dislocations is the diminution of the influence of impurities on annealing-out of point defects.

It has been described previously that concentrations of point defects and dislocations in thorium would be increased with increasing carbon content or deformation. The increases in point defects and in dislocations could be proportional to each other. The independence of the percentage recovery of both stage II (above 80°K) and stage III for deformed thorium from carbon content and the amount of

deformation may possibly verify this assumption. The stage II recovery above 80°K can be divided into two regions. The first region is from 80° to 150°K and the second region is from 150° to 240°K. Because of the increase of percentage recovery with increasing carbon content in the first region of stage II in Figure 6, it is possible that detrapping of interstitials from carbon atoms may occur in this temperature range. Therefore, the stage II recovery peak at 200°K (the second region of stage II) may be only contributed by detrapping of interstitials from other impurities (possibly O, N, or other substitutional impurities). This interpretation is consistent with the fact that there are more than 200 wt. ppm of other impurities than carbon in the thorium specimens. It is reasonable only if the interstitial-O and -N atom complexes have larger binding energies than that of the interstitial-C atom complex. Without knowing the binding energies of various interstitial-impurity complexes, however, this interpretation is only tentative.

Activation Energy and Interpretation of Stage III Recovery

The ratio-of-slope method was used to determine the activation energies for migration of defects in stage II_C and III in both irradiated and cold worked specimens. This

method has the important advantage that the requirement of identical defect configurations at two temperatures is fulfilled automatically. All other methods necessitate the use of two or more specimens, thus having the disadvantage that all specimens must have identical initial defect state. In many cases, because of background annealing, the resistivity values at which a given annealing stage begins and ends cannot be determined precisely (especially the limiting value $\Delta\rho_{\infty}$ of the isothermal annealing). Also, the total amount of recovery in stage III often varies from specimen to specimen even for identical irradiation conditions, especially at low defect densities. Therefore, despite the high accuracy claimed elsewhere (26), the somewhat different values deduced for E_{III} by using the MB and the cross-cut methods are not particularly surprising. Likewise, the graphical method used for the determination of the exponent n in the empirical kinetic equation has problems on reliability and reproducibility. All experimental results indicate that migration of the same type of point defects is responsible for recovery in the latter stage in both cold-worked and irradiated specimens. This conclusion is based on the following observations: (1) The same activation energies were obtained using the ratio-of-slope method. (2) The stage III recovery from both cold-worked and irradiation falls in the same temperature range (250-400°K),

and (3) the recovery curves have the same structure featuring one main peak at 315-330°K.

The stage III recovery cannot be related to the migration of extrinsic impurity atoms (such as carbon atoms) because of the great enhancement of this stage observed in irradiated pure thorium instead of Th-C alloy specimens. Furthermore, the migration energy for diffusion of carbon atoms in α -Th has been estimated to be 1.62 eV (75), which is too high in comparison with the deduced values of activation energy for stage III. Since migration and detrapping of interstitials have been assigned to stages I and II, then vacancy (mono- or di-vacancy) migration might be a logical choice for stage III recovery.

Unfortunately, the experimental value for the activation energy of single vacancy migration in thorium is still not available. The activation energy for self-diffusion, E_{d*} , (equal to the formation and migration energies of single vacancies) of the fcc α -Th, is reported at 77.6 kcal/mole (3.3 eV/atom) (75). A rule of thumb for the estimation of the formation energy of a vacancy, E_V^F , in the fcc metals is above 1 eV per 1000°C of the melting point. This estimation is generally valid to within 10%. Based on this rule, $E_V^F = 1.75$ eV for Th. Taking the difference between E_{d*} and E_V^F gives $E_V^M = 1.55$ eV for the migration energy of single vacancies in α -Th.

Flynn (76) has derived a theoretical expression for diffusion jump in a monatomic crystal:

$$v = \left(\frac{3}{5}\right)^{1/2} v_D \exp[-C\Omega^2/kT] \quad (12)$$

where v_D is the Debye frequency, Ω the atomic volume, and C an average elastic constant for migration calculated from

$$\frac{15}{2C} = \frac{3}{C_{11}} + \frac{1}{C_{11}-C_{12}} + \frac{1}{C_{44}} \quad (13)$$

where C_{11} , C_{12} , and C_{44} are the three independent elastic constants for cubic metals. The quantity $\phi = C\Omega^2$ plays the part of a Gibbs function for migration. For thorium, the following data were suggested: $C = 6.02 \times 10^{10}$ N/m², $\Omega = 3.29 \times 10^{-29}$ m³/atom, $v_D = 10^{14}$ sec⁻¹, and $\delta^2 = 0.104$. The theoretical estimation of migration energy, therefore, can be obtained by combining eq. (12) with the following diffusion expression for fcc crystals,

$$v = \frac{6}{a^2} D_0 \exp[-E_V^M/kT]. \quad (14)$$

Using $a = 5 \times 10^{-8}$ cm, $D_0 = 2100$ cm²/sec for thorium, and $T = 400^\circ\text{K}$, the theoretical value for E_V^M is estimated to be 1.65 eV. This value seems to be reasonable when compared with the value obtained from considerations involving self-diffusion. Both calculated values of E_V^M , however, are about

0.5 eV greater than the activation energy obtained for the stage III recovery. If the latter activation energy is an indication of the defects involved in the mechanism dominating this recovery stage, the deduced value of $E_{III} \sim 1.15$ eV would imply that single vacancy migration is not responsible for the stage III recovery in Th.

Because point defects induced by deformation at low temperatures are produced in rows, according to most models, many of the vacancies thus generated might lead to the formation of divacancies. For fast neutron irradiation, only relatively few defects (vacancies and interstitials) are produced in isolated forms, others in the displacement cascades are more or less correlated or clustered.

According to Schilling et al. (22), because of the greater mobility of free interstitials than vacancies at 80°K, isolated vacancies have a great chance to be annihilated by moving interstitials. On the other hand, the arrangement of point defects in the defect zones tend to bring vacancies together in di-, tri-, and multi-vacancy forms. Also, the very presence of vacancies in the interior of defect zones would enhance their chances of survival from recombinations during irradiation and thermal annealing prior to stage III. Therefore, for fast neutron irradiated thorium, presence of rather high concentration of vacancy complexes (divacancy, trivacancy, ...) below stage III is conceivable.

Although the migration energy of divacancy, E_{2V}^M , has not been evaluated experimentally for thorium, Table 5 shows the experimental values of migration energies for both single vacancies and divacancies in typical fcc metals (77). The estimated migration energy for single vacancies and the observed stage III activation energy for thorium are also listed in this table. An examination of these values and the ratios of E_{2V}^M/E_V^M reveals that while E_V^M and E_{2V}^M values vary widely by a factor of more than two, the E_{2V}^M/E_V^M ratios fall in a close range 0.60 to 0.80. More importantly, the identification of the deduced activation energy of

Table 5. Migration energies of single vacancy and divacancy for fcc metals

	Al	Ag	Pt	Cu	Ni	Au	Th
E_V^M (eV)	0.62	0.83	1.38	0.85	1.40	0.90	(1.65) ^a
E_{2V}^M (eV)	0.42	0.57	1.10	0.71	0.85	0.71	(1.15) ^b
E_{2V}^M/E_V^M	0.68	0.69	0.80	0.84	0.61	0.79	0.70

^aCalculated from Flynn's theory.

^bObserved activation energy for stage III recovery in both cold-worked and neutron-irradiated Th.

1.15 eV with the migration energy of divacancies in Th yields a E_{2V}^M/E_V^M ratio of 0.70, which lies in the middle of the range. This may in part support the tentative interpretation that the stage III recovery in Th is due mainly to the migration of divacancies.

As has been mentioned before, the activation energy E_{III} was found to decrease slightly with increasing carbon content. Several possibilities may be cited for the carbon effect. One was proposed by Lazarus (78) that the impurity atoms tend to form complexes with vacancies, especially when the impurity atoms are multivalent. According to the latter author, the complexes can diffuse more rapidly than single vacancies. Should the Lazarus mechanism be valid, the migration energy would have been lowered as the total impurity concentration increased. Applying this model to thorium, an enhancement of the stage III recovery would be expected in the Th-C alloys. This expectation has not been observed, however. Therefore, the impurity-vacancy complex model must be ruled out.

Another possibility is that proposed by Koehler (77), who invoked the model of divacancy migration in an attempt to explain results obtained from quenching experiments conducted on gold. Koehler's model involves the following assumptions: (1) changing the state of purity would change the sink density C_s , (2) C_s would depend on yield stress at

some critical temperature, and (3) the yield stress would increase as the impurity concentration increases. The increase in excess resistivity with increasing carbon content in thorium has been discussed previously and carbon atoms were proposed as nucleational traps for defects. Therefore, changing the carbon content of thorium specimens would change the sink density. It was also discussed that in cold-worked thorium specimens, the presence of carbon atoms increases not only the concentration of point defects, but also that of dislocations, which are the primary sinks for defects. Peterson and Skaggs (63) have observed that increasing carbon content in thorium tends to increase the yield stress. They also observed an increase in yield stress with decreasing temperature with an upper critical temperature at about 423°K. Hence, the assumptions for Koehler's divacancy-migration model are quite feasible for thorium. This may also support the tentative interpretation of the stage III recovery based on the migration of divacancies.

In neutron irradiated thorium a fraction of the excess resistivity remained after completion of stage III, indicating the retention of radiation-induced defects after stage III. The fraction of remaining damage increases as the carbon content is increased. This might be due to the formation of defect clusters at carbon atoms which act as

nucleational traps. It is also possible that divacancies might be trapped by carbon atoms during the migration as observed by Sorensen (79) in his neutron-irradiated nickel. In cold-worked specimens, the carbon effect on defect retention is not observed. One good reason for this is that the presence of the high concentration of dislocations, being effective sinks for defects, may mask the influence of carbon atoms. The influence of dislocations on the annealing-out of point defects has been described by van den Beukel (41). The latter worker also assumed that 55% of the total increase in resistivity in Cu during low temperature deformation is due to point defects. If a similar contribution from point defects to $\Delta\rho_0$ is envisaged for thorium specimens, then, at the end of stage III, more than 20% of the induced resistivity contributed by point defects would still remain. The remaining point defects may be mainly large clusters which eventually collapse to form dislocation loops or to dissociate at higher annealing temperature.

From the foregoing discussion, it may be concluded that stage III recovery for both neutron-irradiated and cold-worked thorium is possibly due to the migration of divacancies.

Finally, data obtained from the stage III isothermal annealing do not fit the simple rate equation. Rather, they fit the Johnson-Mehl empirical equation. Although the

$\alpha(\text{sec}^{-1})$ value in the Avrami equation is not a true rate constant, its value varies sensitively with the conditions of specimen and annealing temperature. For instance, the observed increase of α value with increasing annealing temperature for irradiated thorium shows the increase of the initial annealing rate. It was also observed that the α value deduced from annealing at 310° and 320°K is decreased by the presence of carbon atoms in the lattice. The latter result implies that at these temperatures the initial annealing rates were suppressed by carbon atoms. The decrease in α value due to impurity was also found in neutron irradiated V and Mo (32). The suppression of the initial annealing rate, however, disappeared when the annealing temperature was increased to 335°K . This change of α with carbon content may be due to the difference in sink distribution at the beginning of stage III recovery. The exponent, n , value is generally related to the nature and/or density of sinks. The difference in the n value between pure Th and the Th-C alloy is not obvious. However, for isothermal anneal at 335°K , the n values for irradiated and cold-worked specimens are 0.43 and $0.5 \sim 0.6$, respectively. In fast neutron-irradiated specimens the main sinks for divacancies might be the interstitial clusters or other defects, whereas in cold-worked specimens they might be dislocations.

SUMMARY

The damage induced in thorium by both fast neutron irradiation and cold work at liquid nitrogen temperature is increased with increasing carbon content. The activation energy of stage II annealing for cold-worked thorium is 0.61 ± 0.07 eV, and this value decreases as the carbon content increases. The migration of detrapped interstitials from impurities is proposed to be the dominant mechanism in stage II_C recovery. For irradiated specimens detrapped interstitials migrate to form clusters or to recombine with vacancies, whereas for cold-worked specimens detrapped interstitials migrate to dislocations.

The migration energy of single vacancies in thorium is calculated to be 1.65 eV. The activation energy of stage III annealing is determined to be $1.16 \text{ eV} \pm 0.08 \text{ eV}$ for cold-worked thorium and $1.14 \text{ eV} \pm 0.04 \text{ eV}$ for neutron-irradiated thorium by the ratio-of-slope method. The activation energy is deduced to be 0.98 eV for irradiated specimens by the MB method. The inconsistency may be due to the inherent experimental error of the methods, especially the MB method.

Because the stage III annealing for both cold-worked and irradiated thorium has the same activation energy, the same temperature range (250-400°K) and the same structure with one peak at 315-330°K, we conclude

that migration of the same type of point defects may be the dominant mechanism. Divacancy migration is chosen as the possible mechanism in stage III recovery for the following reasons: (1) the observed activation energy seems to represent the migration energy of divacancy in view of the E_{2V}^M/E_V^M ratio for various fcc metals. (2) A divacancy-migration model can explain the observation that the activation energy decreases with increasing carbon content. (3) Defect retention (more than 20% and 27-35% of the initial damage production for cold-worked and neutron-irradiated thorium, respectively) above stage III is observed.

The stage III anneals do not fit the simple chemical rate equation, but they can be described by the Avrami empirical equation. The difference in the exponential n value may be due to the difference in sinks; for irradiated specimens divacancies may mainly migrate to interstitial clusters or other defects, whereas for cold-worked specimens dislocations might be the main sinks for divacancies.

It is recommended that in order to get a comprehensive knowledge about the recovery behavior of thorium, quench experiments are needed. Experimental values for migration energy of single vacancy and divacancy in thorium should be established. Our current knowledge about defect-impurity interactions is incomplete to obtain a better explanation

of the effect of carbon atoms on the thorium recovery behavior. Therefore, more work in this field is needed. Furthermore, study of stage IV recovery may also be found fruitful in confirming the stage III recovery mechanism proposed here.

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