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ANNEALING OF NEUTRON-IRRADIATED
VANADIUM CONTAINING OXYGEN

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Based on a M. S. thesis submitted to Iowa State University

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Annealing of neutron-irradiated
vanadium containing oxygen

by

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INTRODUCTION

In recent years, investigations of the post-irradiation properties of metals have increasingly made clear the fact that impurities in a base metal play a significant role in determining the properties of the metal following irradiation. This has been found to be especially true in the case of the group Va metals, which have a relatively high solubility for the interstitial impurities carbon, oxygen, nitrogen, and hydrogen. However, the results and interpretations of the investigations to date have led to considerable controversy concerning the mechanisms responsible for the processes apparently associated with these interstitial impurities, particularly in the case of the prospective reactor metals vanadium and niobium (1-3). The present study was carried out to clarify the role of interstitial oxygen in irradiated vanadium by measuring the activation energy of the $0.2 T_m$ recovery stage in well-characterized samples, where T_m is the melting temperature in degrees Kelvin.

Radiation damage in the metal lattice structure as a result of energetic particle irradiation manifests itself in the form of point defects and point defect aggregates. Final damage configurations may consist of vacancies, interstitials, interstitial-vacancy complexes, dislocation loops, bubbles, voids, or a combination of these, depending on the nature of the bombarding particle, irradiation temperature and fluence, and structure and composition of the material suffering irradiation. This disorder generally reflects itself in the increase of electrical resistivity and, although this property is not directly discriminant with regard to the nature of the various defects, it has become the principal

investigative tool in radiation damage studies due to its sensitivity and convenience. Further information has also been provided via internal friction measurements, as well as occasional measurements of lattice parameter, length, microhardness, stored energy, and magnetic aftereffect.

The gradual return of pre-irradiation resistivity at progressive annealing temperatures has identified five main recovery stages for both face-centered cubic (f.c.c.) and body-centered cubic (b.c.c.) metals. These recovery stages are classified, despite a lack of theoretical basis, according to their homologous temperatures to facilitate comparison and evaluation. Thus it should be borne in mind that the recovery mechanism attributed to a given stage of a particular metal need not necessarily apply to the same stage in another--especially if their crystal structures are dissimilar.

Though most of the early work on radiation effects centered on f.c.c. metals, b.c.c. metals have attracted much interest in recent years. Candidates for first wall materials in advanced reactors, specifically the group Va metals vanadium and niobium, have received special attention due to their fairly high melting points and low neutron cross sections.

Numerous investigations have shown that irradiated and cold-worked b.c.c. metals exhibit a pronounced resistivity recovery stage at about $0.2 T_m$. This recovery stage is sometimes referred to as "Stage III" annealing (see, for example, 4-8), somewhat in analogy to the stage designated Stage III in copper (9). Since the annealing stage at $0.2 T_m$ of interest in this investigation may be associated with quite a different

mechanism from the Stage III in copper, the author shall refer to the investigated annealing stage in vanadium as "0.2 T_m annealing."

Due to the unwieldy amount of literature generated in recent years in the area of radiation damage and damage recovery, the author shall limit his survey to 0.2 T_m recovery in b.c.c. metals, in order to set a proper background for the present work. The 0.2 T_m recovery for irradiated α -iron and the group VIa metals molybdenum and tungsten will be covered, though the emphasis will be placed on the group Va metals niobium and vanadium.

The earliest published work on damage recovery in b.c.c. metals was that of Kinchin and Thompson (10), who identified recovery stages for neutron irradiated molybdenum and tungsten. Recovery processes were observed with activation energies of 0.25 and 1.3 eV for molybdenum and 0.5 and 1.7 eV for tungsten. The first recovery stage in each metal was attributed to interstitial migration to either vacancies or impurity atoms. The second stage was attributed to vacancy-interstitial annihilation via the motion of single or clustered vacancies to trapped interstitials. That a similar annealing spectrum in molybdenum could be produced by cold working at room temperature was shown by Martin (11). The main peak at 150°C (0.15 T_m) yielded a similar activation energy of 1.26 ± 0.04 eV.

A later more detailed investigation by Thompson (12) of the electrical resistivity changes upon annealing of tungsten irradiated at 4°K identified four stages of recovery. The third stage, occurring at 400°C with an activation energy of 1.7 eV, was attributed to vacancy migration.

This conclusion was based primarily on three observations: (i) vacancy migration is generally assumed responsible for "Stage III" recovery in quenched f.c.c. metals; (ii) it is generally established that there is a relation between self-diffusion activation energies and melting temperature, where vacancy formation and migration is the assigned mechanism; (iii) the ratio of activation energy of $0.2 T_m$ annealing to absolute melting temperature is a given metal, or from element to element, varies little with damage mode (i.e., quenching, cold work, irradiation).

Vacancy migration was again proposed as the mechanism for Stage III recovery by Peacock and Johnson (4), who found an activation energy of 1.25 ± 0.08 eV for neutron irradiated molybdenum. However, their conclusions were later contested by Nihoul (13), whose analysis of their data indicated second order kinetics, incompatible with processes involving migration to fixed sinks. His analysis was subsequently corroborated by Schultz (14) and Moteff and Smith (15), who abandoned the vacancy migration mechanism in favor of an intrinsic bimolecular annealing process involving the migration of free interstitials to relatively stable vacancies. This mechanism was supported by electron irradiation experiments on molybdenum by DeJong and Afman (16), who found a pronounced and singly activated stage without an "undershoot effect," which occurs when the electrical resistivity decreases upon annealing to a value lower than the preirradiation resistivity of fully annealed specimens, indicating a nonintrinsic mechanism. Further evidence was supplied by the field ion microscope observations of Attardo and Galligan (17), who observed the annihilation

of self-interstitials in the course of $0.2 T_m$ annealing of very pure irradiated tungsten, with vacancies surviving to higher temperatures.

The most recent conclusions (18) with respect to $0.2 T_m$ recovery in molybdenum and tungsten are: (i) it is an intrinsic mechanism, essentially singly activated; (ii) it involves migration of interstitials in a temperature range where vacancy migration is thought unlikely; (iii) its kinetics are in good agreement with that of bimolecular kinetics.

Due to the high solubility of α -iron and the group Va metals for interstitial impurity atoms, and their association with $0.2 T_m$ recovery, an intrinsic recovery mechanism was found to be questionable. The Brookhaven study (19-22) of irradiated α -iron concluded that carbon plays a major role in $0.2 T_m$ recovery of this metal. Specifically they found: (i) a rapid decrease in Snoek damping attributed to carbon at about $0.15 T_m$; (ii) continuous recovery with no peaks in irradiated specimens containing 0.003% carbon. The importance of conducting investigations on highly purified material was emphasized by Cuddy and Raley (7), who found that a recovery stage associated with $0.2 T_m$ recovery occurs in cold worked iron only if it has been contaminated with carbon. Furthermore, (i) the activation energy of this stage is 0.87 eV, the value for carbon migration in α -iron; (ii) only for iron with less than 1 ppm carbon was no recovery stage observed; (iii) the recovery stage occurred at about the same temperature and about the same rates as that observed by Fujita and Damask (20), implying that aging after straining may be very similar to aging after irradiation.

Investigations of the $0.2 T_m$ recovery mode in the group Va metals vanadium, niobium, and tantalum also pointed to a marked dependence on interstitial impurity content, in contrast with the behavior of the group VIa metals. The first work on neutron irradiated niobium, by Peacock and Johnson (4), revealed a prominent recovery stage at 120°C ($0.14 T_m$) with an activation energy of 1.22 ± 0.02 eV. This stage was interpreted in terms of vacancy trapping by interstitial impurity atoms or annihilation at defect clusters. Meanwhile, Gregory (23) observed that $0.2 T_m$ recovery in cold worked niobium increases with increasing interstitial impurity content.

Köthe and Schlät (24,25) carried out combined impurity doping and plastic deformation experiments on niobium, tantalum, and vanadium utilizing measurements of electrical resistivity, internal friction, modulus defect, and anelastic aftereffect. They found that: (i) the resistivity enhancement of wires after deformation degrees of about 50% was linearly proportional to interstitial impurity content (carbon, nitrogen); (ii) the resistivity enhancement is larger in impure specimens for modest deformation degrees, with the effect attenuating at increasing deformation degrees; (iii) the height of the oxygen Snoek peak decreases in the $0.2 T_m$ range; (iv) only oxygen doped samples exhibit $0.2 T_m$ recovery. Thus, they concluded that the interstitial impurity atoms (IIA's) migrate to dislocations produced by plastic deformation. This effectively removed the IIA's from solid solution which causes a decrease in electrical resistivity and Snoek damping.

A further study on plastically deformed niobium and tantalum was conducted by Johnson (1), who came to quite different conclusions. Isochronal anneals were performed on two sets of niobium wires which were plastically deformed up to 12% in tension. One set had been recrystallized at 1325°C following a 90% reduction by wire drawing; the other had merely been stress-relieved at 700°C following a similar reduction. The impurity concentrations (4) were given as 500, 100, and 50 wt ppm of oxygen, carbon, and nitrogen, respectively. They found: (i) an activation energy of 1.25 ± 0.02 eV for both types of wire; (ii) a given tensile strain produces more $0.2 T_m$ recovery in a stress-relieved specimen than in a recrystallized specimen. They concluded that the higher density of dislocations in the stress-relieved material gave rise to a greater number of point defects generated by dislocation intersection during the subsequent strain. They proposed an intrinsic mechanism involving the migration of point defects, vacancies in particular.

The effect of oxygen on $0.2 T_m$ annealing in neutron irradiated niobium of varying impurity content was investigated by Williams et al. (8). They correlated the decrease of the oxygen Snoek peak during isothermal annealing at 150°C with the electrical resistivity decrease at that temperature and found similar kinetics. They also noted: (i) at less than 4 wt ppm O_2 , a pronounced resistivity stage did not occur; (ii) an "undershoot effect" was observed for oxygen-bearing specimens, i.e., resistivity dropped below the pre-irradiation value for these samples during $0.2 T_m$ annealing; (iii) their measured activation energy of ~ 1.2 eV agrees with that for motion of oxygen in niobium (1.2 eV). On the basis

of these observations, they concluded that the observed annealing stage was due to the migration of oxygen to radiation produced defect clusters.

Studies of recovery phenomena in both neutron irradiated and cold worked vanadium in recent years have yielded incompatible results which have resulted in two quite different suggestions as to the controlling mechanism in the $0.2 T_m$ recovery range: those favoring an intrinsic recovery mode, and those favoring a recovery mode due to migration of interstitial impurity atoms. Surprisingly, the results of the investigations are quite self-consistent within the two groups, and the arguments themselves are of apparent equal virtue (1-3).

Perepezko et al. (26) reported recovery stages at about 170°C in both plastically deformed and fast neutron irradiated vanadium. The impurity concentrations of the samples were 520, 266, 320, and 9 wt ppm of carbon, oxygen, nitrogen, and hydrogen, respectively. The recovery stages after cold working and after irradiation were identical and had an activation energy of approximately 0.8 eV. They observed: (i) this activation energy is significantly different than that for motion of carbon, nitrogen or oxygen in vanadium, thus ruling out an impurity migration recovery mechanism; (ii) the order of kinetics was 0.9 ± 0.1 , characteristic of defect annihilation at fixed sinks; (iii) vacancy trapping at interstitial impurity atoms can account for the observed dependency of recovery magnitude on interstitial impurity content reported by other investigators; (iv) the number of jumps to annihilation (computed to be on the order of 10^8) was too large to correspond to trapping by a random dispersion of IIA's. On the basis of these observations, they proposed a vacancy migration mechanism for $0.2 T_m$ recovery. Anand et al. (27) did similar

electrical resistivity studies on highly deformed vanadium (99.99%). Their recovery at about 170°C also yielded an activation energy of 0.8 eV, though their reaction order was 2, in contrast to that obtained by Perepezko et al. (26). They suggested that the discrepancy was due to a bimolecular reaction predominating at large degrees of deformation, and favored an intrinsic $0.2 T_m$ mechanism, although they did not rule out the effect of interstitial impurities.

On the other hand, a study by Stanley et al. (28) on the effect of interstitial impurities on the annealing of neutron irradiated vanadium led to the conclusion that $0.2 T_m$ recovery was due to the migration of interstitial oxygen and carbon to radiation produced defects. This conclusion was based on the following observations: (i) the magnitude of the resistivity decrease increased with increasing oxygen and carbon content; (ii) the decrease in resistivity was accompanied by the decrease in the oxygen/carbon Snoek peak in the same temperature range; (iii) they observed an "undershoot effect," contra-indicating a purely intrinsic annihilation mechanism; (iv) the measured activation energy of about 1.2 eV is close to the migration energies of oxygen and carbon in vanadium.

Annealing experiments on deformed niobium as a function of strain and oxygen content were carried out by Szkopiak and Pouzet (29), who found that the increase of resistivity due to plastic deformation is proportional to oxygen content. Furthermore, the amount of $0.2 T_m$ resistivity recovery was also proportional to the oxygen content for a given deformation degree, with no change in resistivity in annealing very low (≤ 5 wt ppm) oxygen samples in the same region. They found the recovery kinetics in agreement with a Cottrell-Bilby mechanism and interpreted their results to

indicate oxygen migration and subsequent formation of Cottrell atmospheres at dislocations. These results are similar to those of Köthe (30), who found evidence for equilibrium atmospheres in strain-aged Ta-O and Nb-O. He also found evidence that normal atmosphere formation was followed by precipitation in samples containing 630 wt ppm oxygen. The activation energies determined for the strain aging process were 1.12 eV for tantalum and 1.14 eV for niobium, in close agreement with the respective migration energies of oxygen in those metals.

A study by McIlwain (31) and McIlwain et al. (32) on the annealing behavior of oxygen doped vanadium after low temperature neutron irradiation yielded similar results for 0.2 T_m recovery. He found: (i) an increase in Snoek peak height and lowering of peak temperature with increasing oxygen concentration and neutron fluence; (ii) agreement between isothermal resistivity and internal friction annealing curves; (iii) an $\exp(-t^n)$ annealing dependence, where n is about 0.5. He suggested short range migration of oxygen to vacancy or interstitial platelets as the recovery mechanism.

Recent investigations by Eto et al. (33,34) confirm the role played by interstitial oxygen in neutron irradiated vanadium. They correlated the change in the oxygen Snoek damping and the lower yield stress with electron microscope observations and found that: (i) the Snoek damping decreases upon post-irradiation annealing up to 200-250°C, and begins to recovery upon annealing above that temperature; (ii) higher fluences and original peak heights gave rise to larger decreases in peak heights due to irradiation, yet higher oxygen concentrations yielded lower decreases in damping upon subsequent annealing; (iii) during this annealing treatment there are no observable changes in microstructure, suggesting that the

observed defect clusters are relatively immobile at this stage; (iv) the higher the fluence, the more stable the observed defect clusters. On the basis of these observations, they concluded that oxygen migrates to the radiation defect clusters below 200°C and goes back into solution above 250°C.

The fact that radiation anneal hardening, a post-irradiation increase in yield stress following annealing at moderate temperatures, occurs in the same temperature range as 0.2 T_m recovery has, in recent years, been mentioned as further evidence in favor of impurity migration during 0.2 T_m recovery. It has been observed in niobium (35-37) and vanadium (32,38-42) and has been found to increase with increasing IIA concentration (42). The magnitude of radiation hardening observed in vanadium as-irradiated at 70-100°C is also observed to increase with increasing oxygen concentration (42,43), which may be correlated with the increased radiation-produced defect cluster density (42,44). Furthermore, strain aging due to oxygen is observed to be retarded in irradiated vanadium, presumably due to trapping of oxygen at defect clusters (45).

From the present survey, it is evident that the evidence concerning the controlling mechanism for recovery in the 0.2 T_m recovery range in the group Va metals is far from conclusive.

The purposes of the present study are to:

1. Establish the effect of oxygen on 0.2 T_m annealing in neutron irradiated vanadium;
2. Determine the activation energy of the recovery; and
3. Examine the results in light of previous work.

EXPERIMENTAL PROCEDURE

Sample Preparation

Samples suitable for electrical resistivity measurements were prepared from 150 grams of electrolytic vanadium crystals with an oxygen concentration of 30 wt ppm oxygen. These were arc-melted into two 50 gram buttons and one 50 gram finger. Appropriate amounts of V_2O_5 were then weighed and encapsulated in high purity vanadium foil, placed beneath the vanadium buttons and arc-melted into fingers; this resulted in three fingers of vanadium with concentrations of about 30, 200, and 600 wt ppm oxygen. These fingers were swaged into wire form of 1.30 mm diameter. From these lengths 8 cm sections were cut. Samples to be irradiated were electropolished in a solution of 20% H_2SO_4 in methanol at 8°C, and annealed at 925°C for 1 hour. Additional swaging, annealing, and electropolishing resulted in a final diameter of 0.92 mm. Reference samples consisted of 9 specimens of each oxygen level, 7 of which were swaged to 1.30 mm, electropolished to 1.20 mm and annealed for 1 hour at 925°C, and 2 of which received treatment identical to those to be irradiated.

Concentrations of nitrogen, oxygen, and hydrogen in the final specimens were determined by means of vacuum fusion analysis. Carbon concentrations were determined by combustion analysis, and substitutional impurity concentrations by means of emission spectroscopy. Results of the impurity analyses are given in Table 1. The final oxygen concentrations for the low-, medium-, and high-oxygen final specimens as given in Table 1 correspond to 61, 271 and 583 wt ppm oxygen, respectively.

Table 1. Impurity concentrations in atomic parts per million as determined by chemical analyses

Impurity	Low oxygen	Medium oxygen	High oxygen
O	194	862	1854
N	4	11	11
C	161	246	170
H	101	202	404
Al	<15	15	<15
Ca	75	20	<20
Cr	<50	<50	<50
Cu	<10	<10	<10
Fe	30	100	30
Mg	<20	<20	<20
Mn	<20	<20	<20
Ni	<50	<50	<50
Si	30	<20	30
Ti	<25	<25	<25

Irradiations

The first irradiation was performed in the central column within the neutron converter of the Ames Laboratory Research Reactor to a fluence of 1.3×10^{18} n/cm² ($E > 1$ MeV) at a temperature of $88 \pm 3^\circ\text{C}$. An aluminum experiment can, with cadmium lining to shield out thermal neutrons, enclosed three aluminum capsules, each containing a 1/4 in diameter, 10 mil thick nickel dosimetry foil and 17 vanadium resistivity samples. Each of the three aluminum capsules was attached to a thermocouple to provide for temperature measurement and lowering and raising of the experiment can.

The second irradiation was performed in the same location to an identical dose of 1.3×10^{13} n/cm² ($E > 1$ MeV). In this case, two thermocouples provided for temperature measurement and positioning of the experiment can. Measurements at sample level indicated a temperature of $73 \pm 1^\circ\text{C}$ over the course of the irradiation, while those higher in the can and possibly in contact with the stainless steel top plug indicated a temperature of about 175°C . In contrast with the earlier irradiation, these thermocouples were placed in stainless steel wells and were not in actual contact with the samples. Due to probable gamma heating in the upper region, the lower temperature was taken as most indicative of the true irradiation temperature. Included in the irradiation package were 12 vanadium resistivity wires whose pre-irradiation resistivities had been determined, 7 vanadium resistivity foil samples, and 72 TEM samples. In addition, two Ni-Al activation wires were placed close to the samples for neutron flux determination.

The primary purpose of the second irradiation was to establish the change in resistivity of samples due to irradiation. In this case, primary potential contacts of vanadium wire were spot welded to the wire samples before irradiation and remained in place for post-irradiation potentiometric measurements.

Measurement Technique

For resistivity measurements, primary potential contacts of 0.15 mm diameter vanadium wire were spot welded to the samples 5 cm apart. These remained with the samples throughout subsequent annealing, effecting a

constant gauge length for a given sample over the course of annealing treatments.

Electrical resistivity measurements were made by the standard potentiometric method using a high precision microvolt potentiometer sensitive to $0.01 \mu\text{V}$. A reversing circuit was used to reduce the effect of spurious thermal emfs. Absolute resistivity measurements are estimated to be accurate to within $\pm 2\%$, mainly due to fluctuations in specimen diameters along their lengths; relative errors are less than 0.1% .

Emf measurements were made at 4.2°K . The specimens were immersed in liquid helium at 1 atmosphere in a narrow-mouth 50 liter dewar. In order to quench the superconductivity at 4.2°K , the specimens were housed in a superconducting magnet operating at 5 kG and capable of 20 kG. A constant current source supplied a current of 0.1 ampere throughout the measurements; a Winchester plug and 12 position switch allowed measurements to be made on 4 samples during each liquid helium dip.

Annealing Procedures

Post-irradiation isothermal anneals at 160, 170, 180, and 190°C and isochronal anneals at 1 hour intervals up to 200°C were conducted in a silicon oil bath. Further isochronal anneals were carried out from 210 to 300°C and from 450 to 600°C on samples sealed in pyrex tubing and vycor tubing, respectively, in <1 atm helium. These furnace anneals were temperature controlled to $\pm 3^\circ\text{C}$, and in contrast to the anneals below 200°C , involved the severing and rewelding of numerous Pt-Pt resistivity leads and some Pt-V potential leads. Each anneal was followed by resistivity measurement at 4°K .

RESULTS

Recovery Data

The isochronal recovery of the irradiation induced resistivity for the high, medium, and low oxygen samples irradiated to 1.3×10^{18} n/cm² ($E > 1$ MeV) is shown in Figure 1. The resistivities were measured at 4.2°K and the change with respect to the as-irradiated resistivities are plotted versus the temperatures at which the samples underwent successive one hour anneals. Note that the low oxygen unirradiated sample exhibits virtually no change in resistivity as a function of increasing annealing temperature. The recovery process for the irradiated specimens occurred between 110 and 220°C, with the lower oxygen samples exhibiting larger decreases in resistivity.

It is seen that beyond about 200°C, another process competes with, and finally, overwhelms the earlier process, resulting in pronounced increases in resistivity. This process can be more clearly seen in Figure 2. It should be pointed out that the surfaces of all the samples appeared to be tarnished following the 600°C anneal, but it is doubtful that the surface condition affected the resistivity. Nevertheless, it is clear from Figure 2 that an increase in resistivity occurred for the higher annealing temperatures and that this effect was more pronounced for the higher oxygen samples. This resistivity enhancement process appeared to inhibit the $0.2 T_m$ recovery stage, resulting in maximum decreases in resistivity between 110 and 200°C of 5.19, 12.27, and 18.66 nano Ω -cm for the high, medium, and low oxygen samples, respectively.

Figure 1. Change in resistivity measured at 4.2°K following successive one hour anneals at the temperatures indicated.

Figure 2. Change in resistivity following successive one hour anneals over the entire span of isochronal annealing temperatures.

The isochronal recovery spectrum is shown in Figure 3. The change in resistivity due to annealing at a specific temperature was divided by the temperature interval between this anneal and the preceding one, and plotted against the average temperature of the two anneals. It is seen that the low oxygen sample has a single peak at around 180°C, while the medium oxygen sample appears to have two peaks, one around 175°C and a smaller one around 125°C. The high oxygen sample appears to have a single peak around 125°C.

The isothermal recovery curves for the low oxygen samples annealed at 160, 170, 180, and 190°C are given in Figure 4, along with the isochronal recovery curve on the right. Here the isothermal recovery is expressed in terms of the fractional decrease in resistivity f , where

$$f = \frac{\rho_0 - \rho(t)}{\rho_0 - \rho_f} \quad (1)$$

where ρ_0 is the as-irradiated resistivity, $\rho(t)$ is the resistivity at time t , and ρ_f is the final resistivity after long time annealing. The quantity f is plotted versus the logarithm of the annealing time. It is assumed that this quantity is directly proportional to the concentration of the entity migrating at that stage. It is seen that the curves below $f \sim 0.7$ appear superimposable upon translation along the $\ln t$ abscissa, implying a singly activated process in this region. The average maximum decrease in resistivity exhibited by the low oxygen samples was 21.2 nano Ω -cm, with the maximum decrease varying from 20.8 to 21.7 nano Ω -cm. The purpose of obtaining two 190°C isothermal annealing curves was to investigate reproducibility of the annealing data at high annealing temperatures.

Figure 3. $\Delta\rho/\Delta T$ taken from the 0.2 T_m region of the isochronal annealing curves in Figure 1.

Figure 4. Isothermal annealing curves for low oxygen (V-61 wt ppm O) neutron irradiated vanadium.

The isothermal annealing behavior of the medium oxygen samples was very similar to the behavior of the low oxygen samples. This is seen in Figure 5, 6, and 7. Again, the curves below $f \sim 0.7$ in Figure 5 appear superimposable upon translation along the $\ln t$ abscissa, but in this case in two groups; the lower 160 and 170°C curves and the higher temperature 180 and 190°C curves. This effect is also present in the low oxygen recovery curves, though to a lesser extent. The average maximum decrease in resistivity for the medium oxygen samples was 18.5 nano Ω -cm, with the maximum decrease varying from 16.87 to 19.97 nano Ω -cm. The maximum decrease in resistivity tended to decrease with increasing isothermal annealing temperature.

In contrast to the low and medium oxygen recovery curves, the recovery curves for the high oxygen samples appear inhibited in the sense that the resistivity decrease does not occur more rapidly for higher annealing temperatures. This is seen in Figures 8 and 9, where in this case the absolute decrease in resistivities are plotted against isothermal annealing time. Again, the initial recovery seems to be competing with another process which accelerates at increasing temperatures, eventually taking over and resulting in pronounced increases in resistivity, as was seen in the isochronal recovery depicted in Figure 1. The average maximum decrease in resistivity for the high oxygen samples was 9.9 nano Ω -cm, with the maximum decrease varying from 13.6 nano Ω -cm at 160°C isothermal annealing temperature and decreasing steadily with increasing annealing temperatures to only 6.3 nano Ω -cm at the 190°C isothermal annealing temperature. A point to be made with regard to the high oxygen recovery curves in Figures 8 and 9 is the possible presence of a plateau in the

Figure 5. Isothermal annealing curves for medium oxygen (V-271 wt ppm O) neutron irradiated vanadium.

Figure 6. Absolute change in resistivity as a function of isothermal annealing time at 160 and 170°C. Illustrates that final change in resistivity for low oxygen samples is independent of annealing temperature.

Figure 7. Absolute change in resistivity as a function of isothermal annealing time for medium oxygen, irradiated and unirradiated vanadium.

Figure 8. Absolute change in resistivity as a function of isothermal annealing time at 160 and 170°C. Illustrates that final change in resistivity ($\Delta\rho_f$) is not independent of annealing temperature.

Figure 9. Absolute change in resistivity as a function of isothermal annealing time at 180 and 190°C. Illustrates the inhibition of $0.2 T_m$ annealing at higher annealing temperatures.

course of the annealing process which occurs between 100 and 1000 minutes for the 160 and 170°C anneals, and between 10 and 100 minutes for the 180 and 190°C anneals.

Pertinent data for the irradiations and anneals are summarized in Tables 2 and 3.

Table 2. Irradiation data summary

	Fluence (n/cm ² , E > 1 MeV)	Irradiation temperature (°C)	
Irradiation #1	1.3x10 ¹⁸	88	
Irradiation #2	1.3x10 ¹⁸	73 ^a	
Resistivity values for irradiation #2 (μΩ-cm)			
	V-61 wt ppm O	V-271 wt ppm O	V-583 wt ppm O
Unirradiated	0.147±0.007	0.532±0.004	1.048±0.026
As-irradiated	0.127±0.006	0.466±0.007	0.976±0.021
Change	-0.020	-0.067	-0.073

^aSee, however, EXPERIMENTAL PROCEDURE, Irradiations.

Activation Energy Determinations

Two methods for determining the activation energies of the 0.2 T_m recovery process were used and will be briefly described here. For a singly activated process (one type of defect or interstitial impurity annealing by a single characteristic process), the annealing rate is proportional to some function of the concentration of the annealing entity, and is governed by

Table 3. Annealing data summary (resistivity values at 4.2°K in $\mu\Omega\text{-cm}$)

	V-61 wt ppm 0	V-271 wt ppm 0	V-583 wt ppm 0
Unirradiated standard samples (average)	0.151±0.007	0.531±0.018	1.060±0.026
As-irradiated samples (average)	0.153±0.007	0.500±0.014	0.999±0.016
Changes upon annealing			
Isochronal (max.)	-0.019	-0.012	-0.005
Isothermal			
160°C	-0.021	-0.020	-0.014
170°C	-0.021	-0.018	-0.011
180°C	-0.021	-0.019	-0.009
190°C	-0.022	-0.017	-0.006

$$\frac{-dC_d}{dt} = K F(C_d) = v_0 \exp(-E_a/kT) F(C_d) \quad (2)$$

Here C_d is the concentration and the rate constant K is expressed in terms of an Arrhenius dependence; v_0 is assumed to be temperature independent and $F(C_d)$ is an undetermined function that depends on the nature of the annihilation event. Since the quantity f is taken to be directly proportional to the fractional concentration, we may substitute f for C_d . Integrating then gives:

$$\int_{C_{d0}}^{C_d} \frac{dC_d}{F(C_d)} = tv_0 \exp(-E_a/kT) = t/\tau(T) \quad (3)$$

where

$$\tau(T) = \frac{1}{v_0} \exp(E_a/kT) \quad (4)$$

If we let the integral on the left be given by $\Psi(f)$, then Equations 3 and 4 give

$$\ln \Psi(f) = \ln t - \ln \tau(T) \quad (5)$$

Thus, if the process is in fact singly activated, then decay curves should be superimposable upon translation along the $\ln t$ abscissa. Furthermore, since

$$\ln \Psi(f) = \ln t + \ln \nu_0 - E_a/kT$$

then

$$\ln t = \frac{E_a}{kT} + \ln (\Psi(f)/\nu_0)$$

Suppose one takes a number of samples that have been subjected to the same irradiation damage and anneals each of them at a different temperature, say, T_1 , T_2 , and T_3 , until the recovery process is complete. For each f value, there will be corresponding times t_1 , t_2 , and t_3 for various annealing temperatures T_1 , T_2 , and T_3 . Thus, a plot of $\ln t_i$ versus $1/T_i$ ($i = 1, 2, 3, \dots$) should give a straight line with slope E_a/k . An obvious drawback to this method is that many isothermal anneals are required to obtain sufficient points to enable a reasonable determination of the activation energy. In this study, four isothermal recovery curves were obtained and used for this analysis, known as the method of cross-cut, after Damask and Dienes (46).

The plots of the logarithm of the annealing time versus the reciprocal of the annealing temperature at a specific amount of recovery for the low and medium oxygen samples are given in Figures 10 and 11. Activation energies were calculated from the slopes after fitting the lines by the least squares procedure. For the low oxygen case, the average value of

Figure 10. Method of cross-cut analysis based on low oxygen annealing data in Figure 4.

Figure 11. Method of cross-cut analysis based on medium oxygen annealing data in Figure 5.

the seven determinations is 1.19 eV with a standard deviation of 0.04 eV. For the medium oxygen case, the average value of the 7 determinations is 1.15 eV with a standard deviation of 0.15 eV. If one considers only those f values below 0.7 as being truly representative of the $0.2 T_m$ annealing stage, as might be suggested in light of the isochronal annealing spectrum (Figure 3), one gets average activation energies of 1.20 ± 0.03 and 1.23 ± 0.09 eV for the low and medium oxygen recoveries, respectively.

It should be noted that while the activation energies of the low oxygen analysis appear independent of fractional recovery, the medium oxygen analysis seems to indicate progressively lower activation energies toward the beginning of the isothermal annealing runs. This probably reflects the recovery substage at about 125°C evident in Figure 3. This peak is almost nonexistent for the low oxygen case, appearing at most as a mere broadening of the prominent 180°C peak. In the case of the medium oxygen isochronal run, however, its presence is apparent. It completely dominates the high oxygen recovery spectrum, except for a slight plateau at 150°C whose reproducibility is uncertain. In short, raising the oxygen content appears to: (i) effect a recovery stage with a peak at about 125°C; and (ii) introduce a resistivity enhancement process which suppresses, and finally, overwhelms the recovery process around $0.2 T_m$.

An alternative method of activation energy analysis, employed by Meechan and Brinkman (47) uses one complete isothermal annealing curve and one isochronal annealing curve for another identical sample. In this case, the isochronally annealed samples were annealed for one hour at 10°C intervals. For each fractional decrease in recovery due to isochronal annealing, the length of isothermal annealing is determined that produces

an equivalent recovery. Since the amount of recovery is determined by $t \exp(-E_a/kT)$, we may write

$$\Delta t_a \exp(-E_a/kT_a) = \Delta t_b \exp(-E_a/kT_b) \quad (7)$$

where t_a and T_a refer to the time interval and temperature of isothermal annealing required to produce recovery equivalent to that of the sample isochronally annealed for 1 hour at 10°C intervals. Grouping the constants, we may express this as

$$\ln \Delta t_a = (\ln \Delta t_b + E_a/kT_a) - E_a/kT_b \quad (8)$$

Thus, we see that a plot of $\ln \Delta t_a$ versus $1/T_b$ (the two variables in equation 8) should yield a straight line of slope $(-E_a/k)$.

The results of the Meechan-Brinkman analysis for the low oxygen case are shown in Figure 12. The average value of the five determinations is 1.23 eV with a standard deviation of 0.07 eV. The results for the medium oxygen case are shown in Figure 13, but are believed to be misleading for reasons which will be discussed. The high oxygen curves did not prove amenable to activation energy analysis.

Figure 12. Meehan Brinkman analysis based on low oxygen recovery data in Figures 1 and 4.

Figure 13. Meehan Brinkman analysis based on medium oxygen recovery data in Figures 1 and 5.

DISCUSSION

The results of the isochronal anneals between 110°C and 600°C contain three salient features with regard to the resistivity. First, there is the 125°C peak in the annealing spectrum (Figure 3) which occurs for the high oxygen case and is also apparent as a "shelf" or "step" in the medium oxygen case; it appears absent or as a slight broadening of the left shoulder of the 180°C low oxygen recovery peak. Second, lower oxygen samples exhibited greater resistivity decreases and recovery peaks in the 175°C range, with the medium oxygen peak falling somewhat lower than the low oxygen peak, and the high oxygen 0.2 T_m recovery peak virtually non-existent. Third, there is the marked resistivity enhancement process that occurs between 200 and 600°C (Figure 2), and is seen to effect larger increases in resistivity for samples of larger oxygen content. The author shall discuss each of these features in turn, and finally, examine the observations with respect to possible recovery models.

There was no single activation energy found for the 125°C recovery peak in the high oxygen sample; the stage appears to be associated with a varying activation energy and does not follow first or second order kinetics. The same may be said for the "substage" appearing from 125 to 150°C for the medium oxygen sample. Similar substages have been reported in the literature. McIlwain, (31) reported a 100°C substage in vanadium doped with 460 wt ppm (144 wt ppm oxygen) oxygen irradiated to a fast neutron fluence of 2.7×10^{18} n/cm² at 80°K. The origin of this substage was not identified. Perepezko (48) found a minor recovery stage at 130°C for plastically deformed vanadium containing 520, 266, and 320 wt ppm carbon,

nitrogen, and oxygen, respectively. Moreover, a small peak at 95°C was found by Murphy (49) in vanadium irradiated to a fluence of 10^{18} n/cm². The samples were prepared from the same stock used by Perepezko. Murphy adds that the minor recovery stage could have been virtually annealed out during the three month irradiation at 60°C. Again, the minor peak did not prove amenable to activation energy analysis.

The 175-180°C recovery peaks were associated with a relatively consistent activation energy of 1.21 ± 0.06 eV. This $0.2 T_m$ recovery peak, reported in the literature and the nominal subject of the present investigation, has inspired spirited debate in recent years (1-3). There are, however, no results to date that parallel those presented here in one major aspect of the observed $0.2 T_m$ recovery; the amount of oxygen present in the samples is inversely related to the magnitude of the $0.2 T_m$ recovery. Since the pronounced resistivity enhancement process occurring beyond 180-200°C has also never been reported in the literature, it falls suspect to interfering with $0.2 T_m$ recovery by either preventing the entity responsible for recovery from participating, simply swamping out the $0.2 T_m$ recovery by virtue of its greater magnitude, or both. The fact that oxygen content in the samples is the most important variable strongly suggests that it plays a decisive role in the resistivity enhancement process as well.

Figure 14 shows the medium oxygen isochronal annealing curve as a resultant of two competing processes. The first, or lower, annealing curve is that which one might expect in the absence of the resistivity enhancement process, which accelerates as temperature is increased and finally overwhelms the preceding stage. The latter process is depicted in

Figure 14. Schematic drawing depicting the medium oxygen isochronal annealing curve as a resultant of two competing processes.

the topmost curve. It is clear from the figure that the isochronal annealing curve for the medium oxygen sample was not able to complete itself in the $0.2 T_m$ annealing region as were the isothermal curves.

The preceding observation provides a plausible explanation for the discrepancy between the results of the Meehan Brinkman activation analysis and the method of cross cut analysis for the medium oxygen samples. Although the medium oxygen isochronal recovery was "abbreviated," the analysis was done assuming fractional decrease toward full annealing. The effect of comparing the isothermal curves to the isochronal curves on an f value basis exaggerates the steepness of recovery of the isochronal curve, yielding greater Δt_a values in the graphical analysis, and hence, a larger determined activation energy.

In discussing the dramatic rise of resistivity at annealing temperatures above 180°C , the author would like to begin by first alluding to some annealing experiments done on this same stock material by A. M. Russell (50). In this case, damage was induced via plastic deformation instead of irradiation. Although the data generated were not amenable to activation energy analysis due to instrument noise, the results clearly indicated that higher oxygen samples exhibited greater decreases in resistivity upon annealing. This suggests that trap and sink characters and distributions probably play a determining role in the extent of $0.2 T_m$ annealing in vanadium.

The next point to consider is the results of the second irradiation (Table 2), which was conducted to measure the change in resistivity due to irradiation. The unfortunate aspect of the irradiation was the uncertainty

in the irradiation temperature. The upper and lower temperature limits for the irradiation temperature represent readings from the upper and lower thermocouples as they were positioned in the irradiation capsule. The lower temperature reading (73°C) came from the thermocouple closest to the samples. The high temperature reading (173°C) came from a thermocouple in virtual contact with the top 1/2 in thick stainless steel capsule plug; gamma heating is suspected of raising the temperature of this thermocouple. This uncertainty aside, it is seen that the samples exhibited a decrease in resistivity, just the opposite of what one would expect after irradiating the fully annealed reference samples. An obvious explanation is that oxygen has been taken out of solid solution during irradiation to the degree that, even allowing for the increase in resistivity due to radiation damage, the net effect is to lower the overall resistivity. This effect is also suggested if one compares the as-irradiated resistivities of the annealed samples with those of the unirradiated reference samples. They are equal within experimental error, suggesting that some process has hidden the anticipated resistivity increase.

Eto et al. (33,34) have reported a decrease in the oxygen Snoek damping for vanadium irradiated to a fluence of 2×10^{17} n/cm² ($E > 1$ MeV) at 60°C. Furthermore, this decrease in damping was greater for higher oxygen samples. They suggested that the clustering of point defects about a proportion of the oxygen atoms effectively removes the interstitial from solid solution. They also observed a considerable decrease in the oxygen Snoek peak upon subsequent annealing up to 250°C, during which

there was no observable change in defect microstructure, and recovery of the Snoek peak upon annealing beyond 250°C.

The shapes of the $0.2 T_m$ recovery curves did not prove to be readily amenable to an analysis of reaction order in most cases. Rate theory dictates that a plot of $\ln f$ or $\frac{1}{f}$ versus annealing time will be linear depending on whether the process is of first or second order, respectively. The plots for the low and medium oxygen 190°C isothermal anneals are presented in Figures 15 and 16. It should be pointed out that the plots of lower temperature anneals versus annealing time yielded ambiguous results, probably due to the influence of the preceding substage, which was quickly annealed out at the higher annealing temperature; nevertheless, the two plots show a tendency for almost the entire $0.2 T_m$ recovery stage to obey second order kinetics, gradually becoming first order toward the end of the stage. For instance, the low oxygen recovery follows second order kinetics until about 175 minutes annealing time, or until about $f = 0.2$; the medium oxygen recovery follows second order kinetics until about 125 minutes, or until about $f = 0.3$. The fact that the $0.2 T_m$ recovery stage appears to follow second order kinetics suggests that two species are involved in the recovery. The first obvious candidate is oxygen, whose activation energy of 1.26 eV (51) is very close to the activation energy determined in this work, i.e., 1.21 ± 0.06 eV. The presence of carbon could likely have served to lower the apparent activation energy of the $0.2 T_m$ annealing stage for the low oxygen sample due to its lower activation energy (1.18 eV) and its presence in comparable concentrations, i.e., 194 at ppm O and 161 at ppm C (Table 1). Since diffusion to unsaturable traps

Figure 15. $\ln f$ and $1/f$ versus annealing time for low oxygen isothermal anneal at 190°C .

Figure 16. $\ln f$ and $1/f$ versus annealing time for medium oxygen isothermal anneal at 190°C .

such as defect clusters would be expected to give rise to nearly first order kinetics, and since no free self-interstitials are expected at these annealing temperatures, the only other candidates for a role in the recovery process are vacancies or unstable clusters. Cluster breakup, however, would not be expected to yield a single activation energy due to a distribution of sizes and associated binding energies which must be overcome to effect cluster annealing.

The mobility of vacancies during the $0.2 T_m$ annealing stage has been a matter of dispute for quite some time. Recent quenching experiments (52) performed on vanadium have shown that 1 hr annealing between 650 and 800°K is required for vacancy-trapped oxygen atoms to return to solid solution. This annealing is accompanied by a decrease in resistivity, indicating simultaneous annealing of the vacancies upon breakup of the single vacancy-oxygen complexes. On the basis of this evidence, the activation energy for migration of single vacancies in vanadium was taken to lie between that of oxygen (1.26 eV) and an upper limit of 2.3 eV.

The results of the present investigation, particularly the activation energy analyses, support the view that oxygen is a primary mobile participant in the $0.2 T_m$ recovery process, probably migrating to relatively stable vacancies and thus providing for the measured decrease in resistivity. However, the possibility of simultaneous migration of vacancies during the $0.2 T_m$ annealing stage cannot be discounted.

SUMMARY

This investigation may be summarized by the following conclusions:

1. Vanadium doped with low and medium amounts of oxygen and irradiated to a fast neutron dose of 1.3×10^{18} n/cm² at about 88°C exhibits a major resistivity recovery stage when annealed between 110°C ($T/T_m = 0.181$ and 200°C ($T/T_m = 0.22$), whose recovery peak occurs at about 175°C.
2. The $0.2 T_m$ recovery process is best described as due to a single process. The activation energy for the process is 1.21 ± 0.06 eV, compatible with the activation energy of migration of oxygen in vanadium, i.e., 1.26 eV. The proposed mechanism is migration of oxygen atoms to vacancies, where they are trapped and lower their contribution to sample resistivity.
3. During irradiation at 88°C, a significant proportion of interstitial oxygen comes out of solution, either by diffusion of oxygen atoms to nearby vacancies or by acting as nucleation sites for interstitial clusters.
4. Anneals at temperatures beyond 200°C act to break up oxygen-defect complexes, releasing oxygen atoms back into solid solution and serving to increase resistivity.

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