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1. Introduction

Annealing stages at about 0.2 T_m (T_m = melting temperature in °K) have now been fairly widely observed in irradiated body-centered cubic (bcc) metals, particularly V, Nb, and Fe (for reviews, see [1-4]). The annealing stages have been observed chiefly by electrical resistivity measurements, but relevant information has also been gathered using transmission electron microscopy, internal friction, yield stress, and strain aging studies. Two quite different mechanisms have been proposed (for discussion, see [5-7]). The first mechanism

attributes the annealing stages to the motion and annihilation of an intrinsic radiation-produced defect, particularly the vacancy. According to the second mechanism, the annealing stages are due to the motion of interstitial impurity atoms (IIA's) at about 0.2 T_m, whereupon they become trapped at radiation-produced defects and defect clusters. This effectively removes the IIA's from solid solution, resulting in a decrease in electrical resistivity. It has also been reported that the annealing stage at 0.2 T_m in V is accompanied by a decrease in the Snoek damping due to oxygen [8-12]. Changes in mechanical properties also appear to be associated with 0.2 T_m annealing (for reviews, see [13-15]). For V, this has been reported to take the form of radiation-anneal hardening [8, 11, 15-23] and retardation of strain aging [24].

In most cases where 0.2 T_m annealing in V was attributed to IIA-trapping, the IIA in question was oxygen. If oxygen motion is indeed responsible for the 0.2 T_m annealing, then the annealing activation energy should be close to the activation energy for diffusion of oxygen in V, which is known to be about 1.26-1.28 eV [25-27]. On the other hand, if lattice vacancies are responsible, the annealing activation energy should approximate the vacancy motion energy. This energy is not well known. Schultz [28] has estimated the vacancy motion energy at about 0.5-0.6 eV, whereas Mondino and Seeger [29] indicate a value between 1.25 and 2.3 eV. Unfortunately, measurements of the activation energy for 0.2 T_m annealing in neutron irradiated V have led to conflicting

results. Perepezko et al. [30] reported a value of 0.79 ± 0.09 eV, whereas Stanley et al. [12] gave 1.2 ± 0.1 eV. The purpose of the present paper is to report briefly on a recent investigation of the activation energy for 0.2 T_m annealing in neutron-irradiated V (for further details, see [31]), which led to a value of 1.21 ± 0.06 eV. Based on this observation and others presented earlier, it appears likely that 0.2 T_m annealing stems from oxygen motion and trapping at radiation-produced defects and defect clusters. A simple saturable-trap model is presented based on this extrinsic mechanism for 0.2 T_m annealing. The model appears to be fairly consistent with the experimental results.

2. Activation energy determination

Electrolytic V crystals were co-arc melted with appropriate amounts of V_2O_5 and the castings intermittently swaged, electro-polished, and annealed for one hour at 925°C to give 0.92 mm diameter wire with concentrations of 61, 273, and 583 wt ppm oxygen, as determined by vacuum fusion analysis. Resistivity samples were cut from the wires and irradiated to 1.3×10^{18} n/cm^2 (E > 1 MeV) at 88°C in the Ames Laboratory Research Reactor. Post-irradiation isochronal and isothermal anneals were conducted, with resistivity measurements at liquid helium temperature. Figure 1 shows the results of one-hour isochronal anneals at 10°C intervals starting at 110°C. We see that the resistivity decreases at first (i.e., below about 170°C) by amounts that increase with increasing oxygen

concentration. At the highest temperatures (i.e., above about 210°C), however, the resistivity increases again, also by amounts that increase with increasing oxygen concentration. The resulting pattern is that the isochronal annealing curves for the irradiated samples decrease at first, reach a minimum, and then increase at the highest annealing temperatures. The depth of the minimum increases with decreasing oxygen concentration. As is discussed more fully in [31], the curves in Fig. 1 may be regarded as representing the sum of two effects: (1) a monotonic decrease in resistivity, which we take to be due to the oxygen trapping, and (2) a monotonic increase, occurring at higher temperatures and of unknown origin. The second effect thus interferes with our observation of the oxygen trapping process. Since this interference occurs least for the lowest oxygen concentration material, further discussion in this paper is concentrated on the low-oxygen vanadium alloy containing 61 wt ppm oxygen. For the range of annealing temperatures displayed in Fig. 1, we see that no change in resistivity was observed upon isochronal annealing of the unirradiated alloy.

A series of post-irradiation isothermal anneals was also conducted at 160, 170, 180, and 190°C. The magnitude of the long-time decrease in resistivity was the same at each annealing temperature, namely 0.021 ± 0.001 μohm-cm for the low-oxygen alloy. The change in resistivity upon irradiation was not measured as accurately, but averages from a number of low-oxygen samples indicated that the

resistivity increase upon irradiation was less than about 0.007 μohm-cm. The fractional departure from complete annealing

$$f = \frac{\rho_o - \rho(t)}{\rho_o - \rho_f} \qquad (1)$$

was calculated as a function of time at each temperature, where ρ_o is the as-irradiated resistivity, $\rho(t)$ is the resistivity at time t, and ρ_f is the resistivity after long-time annealing. Fig. 2 gives an activation energy plot using the method of crosscut, i.e., the annealing time to reach various f values is plotted on a log scale vs the reciprocal isothermal annealing temperatures. The annealing activation energies obtained from a least-squares fit to a straight line are indicated on Fig. 2. The average activation energy and average deviation from Fig. 2 is 1.19 ± 0.04 eV. A determination of the activation energy was also made [31] using the Meechan-Brinkman method [32], based on a comparison of the isochronal annealing curve and each of the four isothermal curves (curves for 160, 170, 180, and 190°C). The result gave 1.23 ± 0.07 eV. Taking an average of the activation energy determinations using the methods of crosscut and Meechan-Brinkman, we may set the annealing activation energy for the low-oxygen alloy at 1.21 ± 0.06 eV. In a similar way, the annealing activation energy for the medium-oxygen alloy was determined to be 1.23 ± 0.07 eV by the method of crosscut. The Meechan-Brinkman method did not give reliable results for reasons that are discussed in [31].

Taken as a whole, it appears that annealing activation energies close to the value of Stanley et al. [12], 1.2 ± 0.1 eV, were obtained in the present work. These values are consistent with the diffusion activation energy for oxygen in V, 1.26-1.28 eV [25-27], and are considerably higher than that obtained by Perepezko et al., 0.79 ± 0.09 eV [30]. This provides a further basis for attributing the 0.2 T_m annealing to oxygen trapping and motivation for devising a simple trapping model.

3. Saturable trap model

We assume that during irradiation defect clusters are produced, but the IIA's are not mobile. Upon annealing at 0.2 T_m the IIA's become mobile and some fraction of them become trapped at the defect clusters and are effectively removed from solid solution. The IIA-traps are, however, saturable. Let n equal the concentration of IIA's in solid solution at annealing time t, and let $n = n_0$ at $t = 0$. Also let the concentration of traps at time t be c, and let $c = c_0$ at $t = 0$. Since the traps are saturable, let x equal the number of IIA atoms necessary to saturate the IIA-traps, assumed all of equal size and trapping effectiveness. Then we may set

$$c = c_0 - \frac{n_0 - n}{x} \tag{2}$$

Also for the basic kinetic equation, we write

$$-\frac{dn}{dt} = \Gamma c x' n \tag{3}$$

where Γ is the IIA jump rate, cx' is the probability per

jump of an IIA being trapped, and $1 < x' < x$. We have taken cx' to be the trapping probability per jump in order to allow for the effect of the non-randomness of the trapping sites. Now, the equation analogous to (1) is

$$f = \frac{n - n_f}{n_0 - n_f} \tag{4}$$

It is convenient to make the substitution

$$\gamma = \Gamma x' \frac{1 - A}{A} c_0 \tag{5}$$

where

$$A = \frac{c_0 x}{n_0} \tag{6}$$

and to consider the two cases: (1) IIA-limited case, where $A > 1$, and (2) trap-limited case, where $A < 1$. For the IIA-limited case, at $t = \infty$, $n = n_f = 0$, and, by (2), $c = c_f = c_0 - (n_0/x)$. For the trap-limited case, at $t = \infty$, $c = c_f = 0$ and, by (2), $n_f = n_0 - xc_0$. Substitution of (2, (4), (5), and (6) in (3) give an integrable differential equation whose solution subject to the above boundary conditions is

$$f = \frac{1 - b}{\exp(|\gamma| t) - b} \tag{7}$$

where for the IIA-limited case ($A > 1$), $b = 1/A$, and for the trap-limited case ($A < 1$), $b = A$. Note that for both cases we expect $b < 1$.

For the present investigation it is anticipated that the trap-limited case applies. From our measurements of the absolute resistivity at 4.2°K of the 61, 271, and 583 wt ppm oxygen samples, we deduce a resistivity contribution of about 5 μohm-cm/at.% oxygen. The decrease of 0.021 μohm-cm upon 0.2 T_m annealing should only correspond to about 42 at

ppm oxygen, which would not remove all the oxygen from solid solution. This is in agreement with the conclusions of Stanley et al. [12], McIlwain et al. [11], and Eto et al. [10] based on measurements of the decrease in the oxygen Snoek damping peak upon post-irradiation annealing.

The best fit values of b and $|\gamma|$ were obtained for the isothermal annealing data at 160, 170, and 180°C. The average of these b values was $\bar{b} = 0.65$. Then using this value for each of the three sets of data, the best fit $|\gamma|$'s were recalculated. Fig. 3 shows the experimental points and the curves fitted to the experimental points using the single value of $\bar{b} = A = 0.65$ and the three values of $|\gamma|$ (or γ since $\gamma > 0$ when $A < 1.$, as indicated by (5)). The values of $\tau = 1/\gamma$ are shown in Fig. 3. The fits of (7) to the experimental points using only one variable separately adjusted for each annealing run appear to be reasonably good. A plot of $\ln \tau$ vs $1/T$ gives an activation energy of 1.17 $\pm$ 0.13 eV, in reasonable agreement with the measured average of 1.21 $\pm$ 0.06 eV cited above. On the other hand, if all of the bulk oxygen corresponding to 61 wt ppm oxygen were participating in the trapping process, we would have expected to deduce a lower value of A than 0.65, since $(n_0 - n_f)/n_0 = 13/61 = 0.22$. It may be the case, in fact, that not all of the bulk oxygen does participate in the trapping process. This is indicated, for example, by the observation [33] that oxygen acts to nucleate the formation of radiation-produced defect clusters. This suggests that some of the oxygen is

clustered and remains associated with the defect clusters. When the defect clusters are annealed away at higher temperatures, some of this oxygen may return to solid solution, as has been observed by internal friction measurements [10,12].

4. Summary

(1) The activation energy for the 0.2 T_m resistivity annealing stage in neutron-irradiated vanadium containing 61 wt ppm oxygen was determined to be 1.21 ± 0.06 eV. This value is reasonably close to the oxygen diffusion activation energy in vanadium of 1.26-1.28 eV. Thus, an extrinsic mechanism for the 0.2 T_m annealing stage involving oxygen migration and trapping at radiation-produced defect clusters is indicated.

(2) A simple saturable trap model for the trapping of interstitial impurity atoms at radiation-produced defect clusters is described. The model is applied to the isothermal annealing curves for vanadium containing oxygen. A good fit to the shape of the annealing curves is obtained, and approximate agreement to the measured activation energy is found. However, the model appears to overestimate the amount of oxygen participating in the trapping process.

5. Acknowledgments

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Figure captions

Fig. 1: Change in electrical resistivity measured at 4.2°K following successive one-hour anneals at the indicated temperatures. Open symbols, irradiated samples; closed symbols, unirradiated sample.

Fig. 2: Activation energy plot using method of crosscut for isothermal annealing measurements on the low-oxygen vanadium containing 61 wt ppm oxygen.

Fig. 3: Fractional departure from completion versus isothermal annealing time. Comparison of the fit of the model with the experimental points.

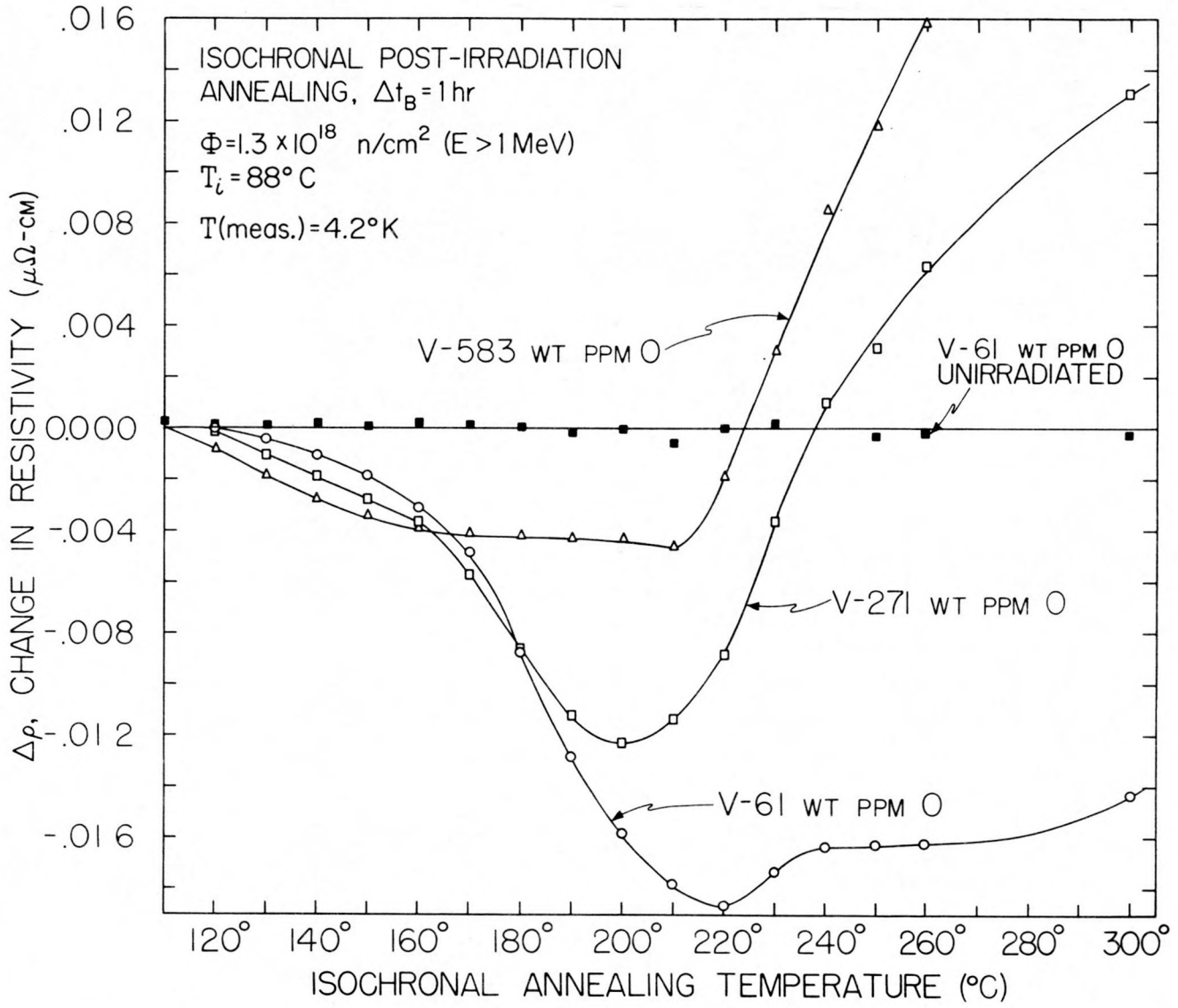
ISOCHRONAL POST-IRRADIATION
ANNEALING, $\Delta t_B = 1$ hr
$\Phi = 1.3 \times 10^{18}$ n/cm^2 (E > 1 MeV)
$T_i = 88°$ C
T(meas.) = 4.2°K
V-583 WT PPM O
V-61 WT PPM O
UNIRRADIATED
V-271 WT PPM O
V-61 WT PPM O
.016
.012
.008
.004
0.000
-.004
-.008
-.012
-.016
$\Delta\rho$, CHANGE IN RESISTIVITY ($\mu\Omega$-cm)
120° 140° 160° 180° 200° 220° 240° 260° 280° 300°
ISOCHRONAL ANNEALING TEMPERATURE (°C)

Fig. 1

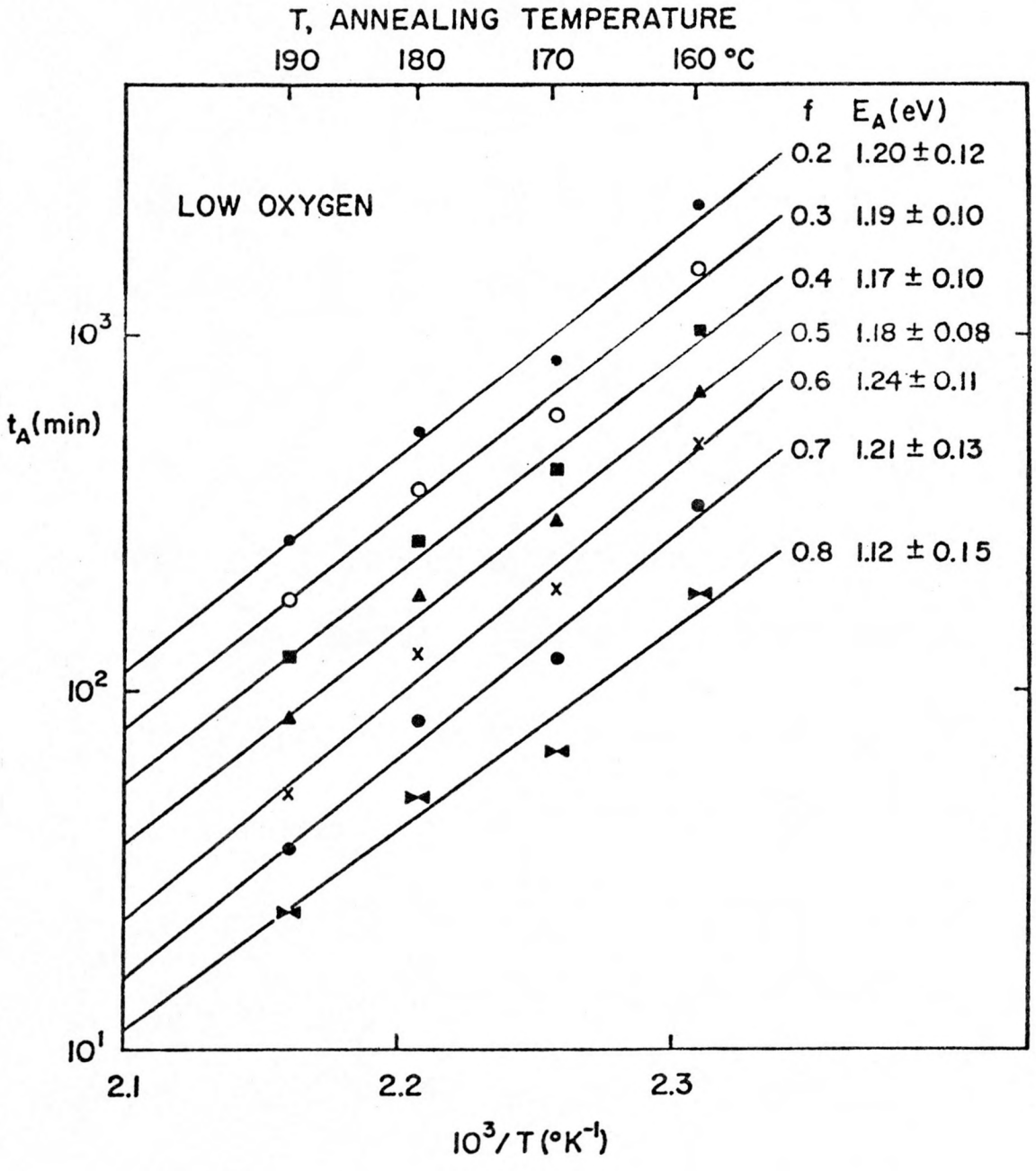
T, ANNEALING TEMPERATURE
190
180
170
160 °C
f
E_A(eV)
0.2 1.20 ± 0.12
0.3 1.19 ± 0.10
0.4 1.17 ± 0.10
0.5 1.18 ± 0.08
0.6 1.24 ± 0.11
0.7 1.21 ± 0.13
0.8 1.12 ± 0.15
LOW OXYGEN
10^3
10^2
10^1
t_A(min)
2.1
2.2
2.3
$10^3/T$ (°K^{-1})

Fig. 2

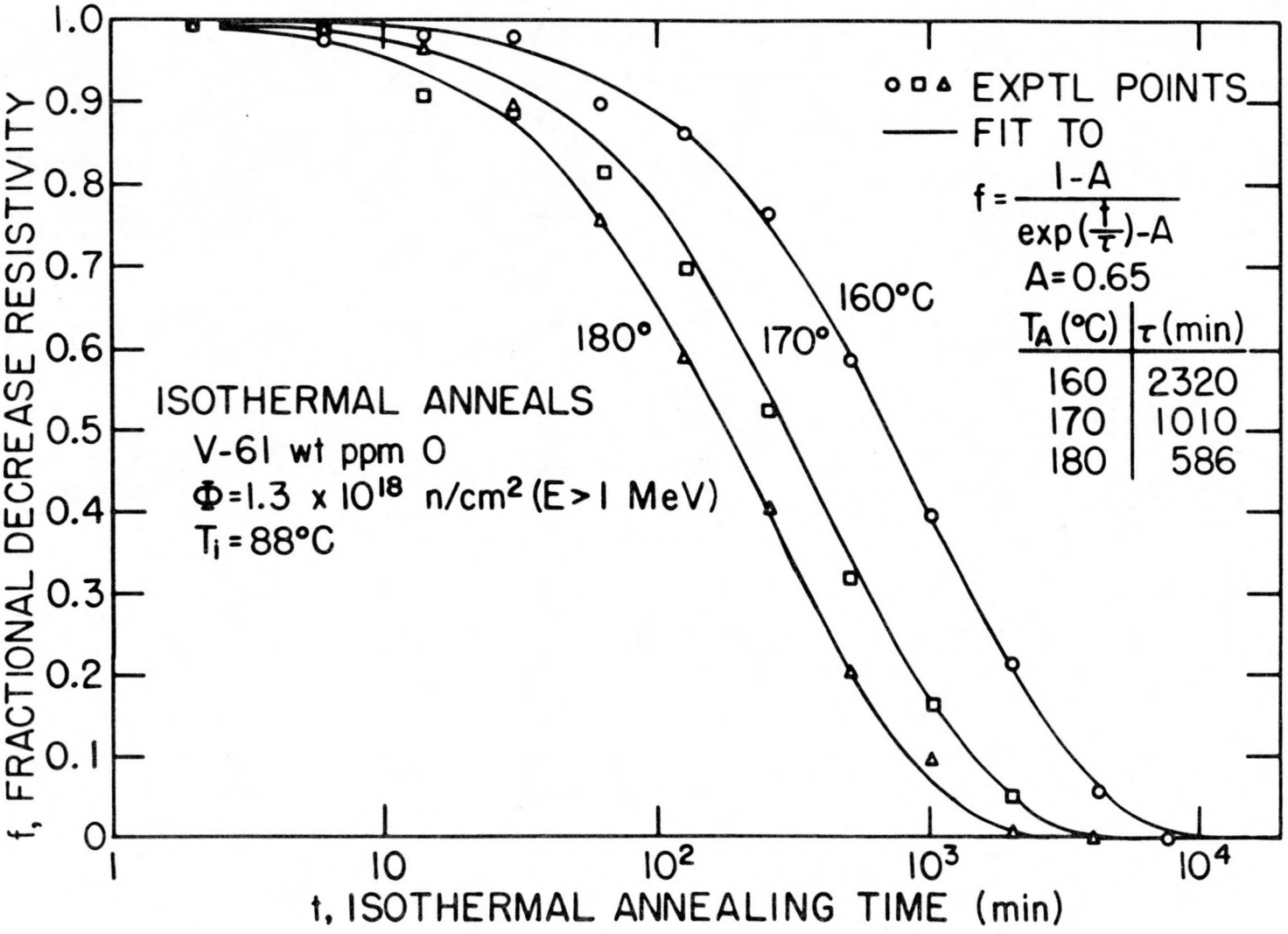
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
f, FRACTIONAL DECREASE RESISTIVITY
1
10
10²
10³
10⁴
t, ISOTHERMAL ANNEALING TIME (min)
ISOTHERMAL ANNEALS
V-61 wt ppm O
Φ=1.3 x 10¹⁸ n/cm² (E>1 MeV)
Tᵢ=88°C
180°
170°
160°C
EXPTL POINTS
FIT TO
f = (1-A) / exp(t/τ)-A
A=0.65
TA (°C) | τ (min)
160 | 2320
170 | 1010
180 | 586

Fig. 3