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ANELASTIC STUDY OF DIVACANCY DAMPING IN GOLD

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June 1970

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BY

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M.S., University of Illinois, 1967

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THESIS

Submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy in Metallurgical Engineering
in the Graduate College of the
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ANELASTIC STUDY OF DIVACANCY DAMPING IN GOLD

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University of Illinois, 1970

The frequency dependence of the damping peak due to divacancy damping in high purity quenched gold was measured. The annealing characteristics of both the divacancy damping peak and the background damping were also investigated. The results of the frequency dependence of the damping peak are discussed in terms of a divacancy rotating in the lattice with an energy of motion of 0.65eV. The results of the annealing study of the damping peak are interpreted as single vacancies coming together to form divacancies giving an initial increase in the divacancy concentration. The divacancies then migrate to sinks causing the divacancy damping peak to disappear. The annealing of the background damping is interpreted in terms of divacancies migrating to dislocations and pinning them. Analysis of this annealing yields a long range energy of motion which is consistent with the rotational energy of motion measured.

An analysis of the annealing of the divacancy damping peak and its height also indicates that a divacancy is tightly bound and has a large dipole anisotropy strength.

ACKNOWLEDGMENTS

The author wishes to express his appreciation to Professor Howard K. Birnbaum for his patience and advice during the course of this investigation and to thank Robert Hoffman for many helpful discussions. The author also wishes to thank Mrs. Janet Franklin for her patience and aid in typing the manuscript.

The support of the U. S. Atomic Energy Commission (Materials Research Laboratory) contract 1198 (1330) during this investigation is gratefully acknowledged.

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I. INTRODUCTION

Since the initial experiments of Bauerle and Koehler (1) demonstrated that vacancies could be quenched into f. c. c. solids, there has been a great deal of work on quenched gold in an effort to determine the parameters which describe the formation and annealing of quenched-in vacancies. Considerable success has been achieved in determining the energies of formation and motion of a single vacancy by combining equilibrium vacancy concentration measurements (2) and self diffusion measurements (3) to yield $E_{lv}^f = .98 \text{ eV}$ and $E_{lv}^m = .84 \text{ eV}$. It has also been shown that the primary sinks for excess vacancies are stacking fault tetrahedra at high vacancy concentrations and low annealing temperatures (4) and dislocations at low vacancy concentrations and high annealing temperatures (5). Our understanding of the kinetics with which excess vacancy concentrations anneal and of the properties of the various vacancy clusters is less than satisfactory. Bauerle and Koehler (1) originally reported annealing kinetics which were characterized by an effective energy of motion which increased from 0.63 eV to 0.82 eV as the quenching temperature was decreased from 1000°C to 750°C. Low temperature transient annealing kinetics were reported by deJong and Koehler after quenches from 1000°C, and these were interpreted (6) on the basis of an annealing model involving mobile single and di-vacancies with a low divacancy binding energy, $E_{2v}^b \approx 0.1 \text{ eV}$. If $E_{2v}^b \approx 0.1 \text{ eV}$, vacancies spend part of their time as single vacancies and part as divacancies as governed by the equation:

$$\tau_{2v}/\tau_{1v} = C_{2v}/C_{iv} = 6C_{iv} e^{E_{2v}^b/kT} \quad (1)$$

where the τ 's are the lifetimes and C 's are the concentrations of the single and divacancies. At high concentrations of vacancies, τ_{2v}/τ_{1v} is large and E_{2v}^m is measured. For lower concentrations, τ_{2v}/τ_{1v} is small and E_{1v}^m is measured. Since high temperature quenches produce large vacancy concentrations, the value of 0.6eV measured by Bauerle and Koehler (1) was associated with the divacancy motion energy E_{2v}^m using the above model. After quenches from low temperatures (i.e. low vacancy concentrations), the low binding energy model suggests that E_{1v}^m is measured and has the value of 0.8eV.

Koehler and deJong (6) extended the above model to determine an effective diffusion coefficient for vacancy complexes diffusing to sinks. They interpreted their measurements as yielding $E_{2v}^m = 0.66\text{eV}$ and $E_{2v}^b = 0.1\text{eV}$. Chick et al. (7) have interpreted a wide range of data and also concluded that a low divacancy binding energy model best fits the data.

In contrast to the above investigations a number of groups have interpreted their results in terms of a high E_{2v}^b model. Ytterhus and Balluffi (8) determined an energy of motion of 0.7eV over a total vacancy concentration range of 1.5×10^{-6} to 5×10^{-5} atom fractions and annealing temperatures between 30°C and 185°C and attributed the annealing to divacancy motion. Their analysis suggested that $E_{2v}^b = 0.3\text{eV}$. Similar results were obtained by Westdrop et al. (9), Mori et al. (10) and

Kauffman and Meshii (11). Recently Wang et al. (5) have studied vacancy annealing kinetics by pulse annealing quenched gold specimens at temperatures as high as 670°C . Using a model employing mobile single and divacancies they obtained $E_{2v}^m = 0.69\text{eV}$ and $E_{2v}^b = 0.4\text{eV}$. A brief summary of the results available to the authors is listed in Table I.

It is clear that while the range of values of E_{2v}^m is small no satisfactory agreement has yet been reached on the value of E_{2v}^b . Most of the arguments so far have depended upon the interpretation of resistivity measurements carried out during the annealing of quenched gold specimens. The annealing kinetics are complex and clearly reflect both the properties of the mobile vacancy species and the characteristics of the sinks. Furthermore, since the annealing occurs in a single broad stage, both single and divacancy migration contribute to the measured decreases in resistivity. As a result, attempts to determine E_{2v}^m from the energy of motion determined from resistivity measurements, E_{eff}^m , will depend on the value of E_{2v}^b assumed.

The complexities of interpretations of the resistivity annealing kinetics suggests that a method of measurement which would be sensitive to only a single vacancy or a divacancy, but not both, would be desirable. One property that distinguishes small vacancy clusters from single vacancies is the symmetry of their strain fields. The vacancy has the cubic symmetry of the f. c. c. lattice while the $\langle 110 \rangle$ divacancy has orthorhombic symmetry. The divacancies can therefore give rise to anelastic and magnetic relaxations (13) while the single vacancy will not.

Table I. Summary of some different investigations of E_{2v}^m and E_{2v}^b .

Investigator	E_{2v}^m (eV)	E_{2v}^b (eV)
de Jong and Koehler (6)	0.66	0.1
Siegel (4)	0.70	
Wang, Seidman, and Balluffi (5)	0.69	0.4
Mori, Meshii, and Kauffman (10)	0.70	≥ 0.3
Kauffman and Meshii (11)	0.71	
Delaplace et al (12)	0.70	
Present work	0.65	≥ 0.3

The interaction of the divacancies with the applied stress (14) results in the reorientation of the divacancies with first order kinetics and an activation energy equal to E_{2v}^m . The magnitude of the anelastic relaxation is proportional to the concentration of divacancies. Measurements of the internal friction should therefore allow a determination of E_{2v}^m and E_{2v}^b .

Neuman (15) and Okuda and Hasiguti (16) have attempted internal friction measurements on quenched gold with little success. The major difficulty in their work appeared to be the small size of the divacancy relaxation and the sensitivity of their results to small deformations. Wuttig and Birnbaum (17) have successfully measured a magnetic relaxation in nickel which they attribute to a divacancy. It is the purpose of this study to investigate the internal friction spectrum in quenched gold in order to obtain some insight into the properties of divacancies.

II. EXPERIMENTAL PROCEDURE

The design of an internal friction experiment to study divacancy properties must take into account the serious problems encountered by previous investigators. In the case of gold one needs to minimize handling and quenching strains while retaining a high quenching speed to avoid significant loss of vacancy defects during the quench. By using thin wires, i. e. diameters on the order of a few mils, one can obtain rapid cooling rates in air and water; of the order of 10^5 °C/sec. for water.

The handling strains can be eliminated if the specimens are quenched in situ and measurements made without remounting the specimens. A method has been developed in which thin wires can be quenched in situ at various quenching rates and damping measurements performed without remounting the specimens. A brief description of the experimental technique is given below. (See Appendix A for a more detailed description of the apparatus).

Specimens shaped in the form of an elongated "U" were suspended in a magnetic field and caused to vibrate in the flexural mode by passing a small a. c. current through the wire at the same frequency as the resonant frequency of the wire. The damping was measured by removing the drive current and applying the output voltage to a high impedance amplifier. The free decay of the specimen produced an output voltage caused by the motion of the specimen wire in the magnetic field. The strains due to flexure, ϵ , are given by Timoshenko and Young (18) as:

$$\epsilon = y/\rho \quad (2)$$

where y = radius of specimen

ρ = curvature of specimen

and for our experiment the maximum strain amplitude was 8×10^{-6} or less. In this strain range the damping was essentially amplitude independent. Since the frequency of vibration is determined by the length and diameter of the wire, the frequency dependence of the damping may be determined by changing either the diameter or the length of the wire. The length and therefore the vibration frequency can be changed in situ by altering the position at which the specimen is clamped. The frequencies used were in the range of 8.5 Hz to 24.3 Hz.

The specimen material was polycrystalline gold wire supplied by Cominco and having diameters of 2 and 4 thousandths of an inch and nominal purities of 99.999% and 99.9999% respectively. The wire was cleaned in acetone, etched in a 50% H_2O -50% nitric acid solution and annealed in air at about $800^\circ C$. After forming the wire in a "U" shape in the experimental apparatus, it was further annealed in situ in air at temperatures of about $1000^\circ C$. Anneals were performed in air in an effort to reduce the vacancy sink density in accordance with the reports of Ytterhus and Balluffi (8). All pre-quench anneals were made using an a.c. current. The specimen temperature was then adjusted to the quench temperature and the specimen was air or water quenched to $23^\circ C$ in situ. All temperatures were measured with a micro-optical pyrometer.

Measurements of the damping were then made as a function of temperature between 115°K and 373°K in a vacuum of better than 10^{-3} torr. The specimen temperature was measured at the specimen clamp using a copper-constantan thermocouple and was accurate to $\pm 1^{\circ}\text{C}$. The damping was measured in free decay in terms of the logarithmic decrement, δ , defined by:

$$\delta = 1/N \ln(A_2/A_1) \quad (3)$$

where N is the number of cycles required for free decay from amplitude A_2 to A_1 .

III. CHARACTERISTICS OF THE DIVACANCY RELAXATION PEAK

The temperature dependence of the internal friction of 0.004 inch diameter gold wires in a slightly deformed condition is shown in Fig. 1. The spectrum (Curve A) is characteristic of specimens which were preannealed at about 800°C and then slightly deformed by shaping into a "U" shaped specimen. The damping was about 7×10^{-3} , and no well defined peaks were observed. The amount of strain received by these specimens greatly exceeded that which might occur during a quench. Annealing at high temperatures and slow cooling reduced the damping to about 3×10^{-3} (Fig. 1 Curve B). In a number of annealed specimens a small damping peak at about -60°C was observed. This peak, which was not observed after quenching, was not investigated. The internal friction was reproducible for measurements taken on heating and on cooling, i. e. no hysteresis was observed in annealed specimens.

After annealing and quenching from high temperatures a small but reproducible damping peak was observed at about 0°C, for frequencies of about 9 Hz. It is this relaxation peak which has the characteristics of the divacancy relaxation peak and which was studied in detail. Typical damping peaks for a specimen which was water quenched from 1015°C and annealed at 24°C are shown in Fig. 2. The peaks were reversible in that they were observed on both heating and cooling, and their shapes are consistent with that expected for relaxation phenomena associated

Figure 1

The internal friction of slightly deformed and of annealed 0.004 inch diameter gold wire versus temperature. Frequency = 16.0Hz.

A. · as strained.

B. * annealed at 950°C for 2 hr. and slow cooled.

with the reorientation of point defects. The agreement of the measured damping with the theoretical curve:

$$\delta = \Delta \frac{\omega \tau}{1 + \omega^2 \tau^2} \quad (4)$$

where Δ = relaxation strength

ω = vibration frequency

τ = relaxation time

is shown in Fig. 2. These peaks do not have the asymmetry which appears to characterize relaxation peaks associated with dislocations (19).

Prolonged low temperature anneals at about 24°C were sufficient to remove these relaxation effects (Fig. 2) completely. The behavior of these peaks on low temperature annealing is consistent with the behavior expected from the theory of point defect annealing as will be discussed later.

During the annealing the background damping was observed to decrease monotonically from the as quenched values of about $\delta = 10^{-2}$ to values of the order of $\delta = 2 \times 10^{-3}$ at 0°C and as low as 2×10^{-4} at -100°C.

These background annealing effects are believed to be due to the pinning of the dislocations by quenched-in point defects as will be discussed in greater detail later.

The relaxation peaks described above were observed only in specimens in which an excess vacancy concentration was retained by quenching. These data are consistent with a stress induced reorientation of a small vacancy cluster such as the divacancy. The relaxation phenomenon is similar to the stress induced reorientation of solute atoms, the Zener Relaxation (20). That these effects were not caused by plastic

Figure 2

Damping spectra for a specimen water quenched from 1015°C with a frequency of vibration of 13.7 Hz. The background damping has been subtracted.

- O Annealed at 24°C for 33 hours.
- Annealed at 24°C for 51 hours.
- △ Annealed at 24°C for 66 hours.
- Theoretical curve normalized for 33 hour anneal run.

deformation may be shown by the following observations: a) The internal friction peaks were not present even when small strains were deliberately introduced (Fig. 1). The use of the present experimental technique and the annealing just prior to the quench should remove even the small handling strains due to mounting the specimens. b) The quenching strains in these small wire diameters are expected to be negligible (21). The peaks were observed both after water quenching and gas quenching. Changes in the surface tension of the quenching bath (obtained by using water-acetone mixtures) had no effect on the damping peaks. c) The relaxation peaks due to deformation, Hasiguiti peaks (19), were never observed in quenched specimens. These peaks generally have an asymmetry (19) which was not observed in any of the divacancy peaks. The annealing characteristics of these Hasiguiti peaks are completely different from the observations which will be reported for the annealing of the divacancy peak. Small amounts of deformation which are known to enhance the Hasiguiti peaks completely mask the divacancy peak.

We may conclude therefore that the internal friction peak which we have observed is not caused by a dislocation effect and may be associated with a small vacancy cluster. It will further be shown that the behavior of the observed internal friction peak is consistent with that expected from divacancies.

After rapidly cooling from an elevated temperature an f.c.c. metal is expected to contain single vacancies, divacancies and small clusters of vacancies. Anelastic relaxations are expected to result

from those defects whose strain fields have a symmetry lower than that of the host lattice. In a quenched f.c.c. metal single vacancies should not produce an internal friction peak while divacancies and higher order clusters may. A divacancy in an f.c.c. metal has a $\langle 110 \rangle$ symmetry axis and its strain field has orthorhombic symmetry. The relaxation of this type of defect has been discussed by Nowick and Heller (14) and Berry (22). Klein and Kronmüller (23) have discussed in detail the case of a divacancy in nickel. In a longitudinal stress field the reorientation of the divacancies leads to two relaxations. As discussed by Klein et al these two relaxations have relaxation times of τ and $3/2 \tau$. Our measurements were unable to resolve these two relaxations, and they both contribute to a single broadened damping peak.

Relaxations may also be observed from trivacancies and higher order clusters whose strain field symmetries are lower than that of cubic. However, since the relaxation strength is proportional to the concentration of the relaxing species, vacancy clusters other than divacancies will give very small relaxation effects. The concentrations of the vacancy defect clusters quenched into the specimens are given by:

$$C_{2v} = 6C_{1v}^2 e^{E_{2v}^b/kT_{eq}} \quad (5)$$

$$C_{3v} = 48C_{1v}^3 e^{E_{2v}^b/kT_{eq}} e^{E_{3v}^b/kT_{eq}}$$

and in general

$$C_{iv} = nC_{1v}^i \prod_{j=2}^i e^{E_{iv}^b/kT_{eq}}$$

where C_{iv} is the concentration of a cluster of i vacancies, n is a geometrical constant, T_{eq} is the temperature where equilibrium is achieved, and E_{iv}^b is the binding energy of a vacancy to the i^{th} cluster. Since C_{iv} is of the order of 10^{-4} or less, the ratio of divacancy relaxation strength to the trivacancy relaxation strength is of the order of 10^{-4} or smaller. On this basis we may conclude that relaxation contributions due to vacancy clusters other than divacancies are negligible.

The relaxation strength of the divacancy peak should vary with the quench temperature in the same way as the divacancy concentration does. After an ideal quench (infinite quenching rate)

$$\delta \propto C_{2v} = 6 e^{-(2E_{1v}^f - E_{2v}^b)/kT_q} \quad (6)$$

where T_q is the temperature from which the quench is carried out. Equation 6 cannot be used to directly determine E_{2v}^b since equilibration of the vacancy-divacancy populations occurs during and after the quench. For a finite quenching rate Equation 6 must be written:

$$\delta \propto C_{2v} = 6 e^{-2 E_{1v}^f / k T_{eq1}} e^{E_{2v}^b / k T_{eq2}} \quad (7)$$

where T_{eq1} is the temperature below which the vacancies are no longer in equilibrium with the vacancy sinks and T_{eq2} is the temperature below which the vacancy-divacancy equilibrium is no longer maintained. Since T_{eq1} and T_{eq2} depend on the quenching rate and are not known, the value

of E_{2v}^b cannot be obtained from the present data using equation 7.

However, the magnitude of the divacancy peak is qualitatively consistent with equation 7 and rapidly increases as the quench temperature is increased. Fig. 3 shows the dependence of the maximum divacancy peak height on quenching temperature after water quenches. A very large increase in the relaxation amplitude with the quench temperature was observed.

The vacancy concentration quenched into a specimen decreases as the quenching rate decreases (24). For any quenching rate the effective quench temperature is that below which equilibrium between the vacancies and sinks is no longer maintained. Slower quenches should allow more time at each temperature for equilibration and therefore produce smaller divacancy internal friction peaks since the number of divacancies is determined by the effective quenching temperature. Gas quenches should therefore produce smaller peaks than water quenches when carried out from the same quench temperature. This is in agreement with the experimental results as shown in Table II. After gas quenches smaller maximum peak heights were observed than after water quenches from the same temperature. The gas quenches performed on 0.002 inch diameter wires had larger damping peaks than those performed on 0.004 inch diameter wires from the same quench temperature which is consistent with the expected quenching rates.

The relaxation strength due to the divacancies, Δ , can be related to the anisotropy of the defect dipole strength, ϵ , and concentration of

Figure 3.

The natural logarithm of the divacancy damping peak maximum $\delta_{\max}$ versus the reciprocal quench temperature, T_q^{-1} .

divacancies, C_{2v} , with the equation:

$$\Delta = T_o / T - T_o \quad (8)$$

where $T_o = C_{2v} \Omega (\delta\lambda)^2 / \beta k J_u$

where Ω is the atomic volume, β is a number of the order of 4 for polycrystalline gold, and J_u is the unrelaxed compliance. Calculation of Δ requires an independent determination of C_{2v} and $\delta\lambda$. However, a lower limit can be calculated for the divacancy dipole anisotropy strength, $\delta\lambda$, if we estimate C_{2v} from the quenching temperature for water quenches close to the melting point. The maximum equilibrium concentration of vacancies at temperatures near the melting point has been shown by Simmons and Balluffi (2) to be about 5×10^{-4} . If losses of vacancies to sinks is neglected and all the single vacancies combine to form divacancies, C_{2v} is about 2.5×10^{-4} . The maximum damping peak height observed on quenching from 1035°C was 8×10^{-3} . The divacancy dipole strength anisotropy can then be calculated using Eqn. 8 to be $\delta\lambda \sim 0.65$. This is a larger value of $\delta\lambda$ than has been calculated by either Schottky, Seeger and Schmid (25) or Yoshida and Koehler (26) from theoretical models of the divacancy structure. Schottky et al. calculate a divacancy dipole strength anisotropy of about $\delta\lambda \sim 0.2$ by representing the crystal energy in terms of the energy of the electron gas and a Born-Mayer interaction energy between ions. The strain field around the divacancy was calculated by minimizing the energy of a small volume

Table II. Effect of quench rate on divacancy damping peak.

Quench medium	Wire diameter (inches)	T _q (°C)	$\delta_{\max}$
Air	0.004	1015	8×10^{-4}
Air	0.002	1025	20×10^{-4}
Air	0.002	1000	18×10^{-4}
Water	0.004	990	7×10^{-4}
Water	0.004	1000	18×10^{-4}
Water	0.004	1015	50×10^{-4}
Water	0.004	1035	80×10^{-4}

around the divacancy and matching the strain field to an elastic dipole strain field at large distances from the divacancy. Yoshida and Koehler have calculated a value of $\delta\lambda = 0.30$ using a hard sphere model of the divacancy. While we can only determine a lower limit for $\delta\lambda$, our measurements indicate a considerably larger relaxation strength for the divacancy damping peak than do the theoretical calculations.

In order to determine the energy of motion of the defect, the temperature dependence of the divacancy damping peak was measured as a function of the vibration frequency. As seen from Eqn. 4 the condition for the damping maximum is given by $\omega\tau = 1$ where $\tau = \tau_0 \text{Exp}(E_{2v}^m/kT)$. The data agrees with this relation as shown by the variation of the frequency versus the reciprocal peak temperature shown in Fig. 4. A least squares analysis of the data in Fig. 4 results in the values:

$$E_{2v}^m = 0.65 \text{ eV} \pm 0.08$$

$$\tau_0 = 0.98 \times 10^{-13} \text{ sec.}$$

The pre-exponential $\tau_0 = \nu^{-1} \text{Exp}(-S_{2v}^m/k)$ where ν is the attempt frequency and S_{2v}^m is the entropy of divacancy motion. Using $\nu^{-1} = 10^{-13}$ sec. results in a value of $S_{2v}^m = -0.02k$.

The value of $E_{2v}^m = 0.65 \text{ eV}$ is in good agreement with the results of Ytterhus and Balluffi (8) and Wang et al. (5) as shown in Table 1. Since the previous measurements determined E_{2v}^m for long range migration, the present results suggest that the long range energy of motion is

Figure 4

The natural logarithm of the frequency of the divacancy damping peak versus the reciprocal measured peak temperature multiplied by Boltzman's constant.

the same as the energy of rotation for the divacancy. This conclusion is different than that obtained for divacancies in nickel (17) where E_{2v}^m (migration) $>$ E_{2v}^m (rotation). In nickel the inequality was ascribed to interactions between the divacancies and impurities while in the case of high purity gold this type of interaction does not seem to be important. Since long range divacancy migration may occur by the same rotational motion that causes the divacancy relaxation, the results obtained in gold are consistent with the expected divacancy behavior in high purity f. c. c. metals.

IV. ANNEALING CHARACTERISTICS OF THE DIVACANCY RELAXATION PEAK

The annealing characteristics of the divacancy peak contains information about the binding energy of the divacancy. The concentrations of single and divacancies immediately after the quench are determined by Eqns. (7) and:

$$C_{iv} = e^{-E_{lv}^f/kT} e^{-1} \quad (9)$$

After the quench the single and divacancies will anneal by coming into equilibrium with each other and with their respective sinks. Damask and Dienes (27) and Meshii, Mori, and Kauffman (28) reported computer analyses of this annealing. Damask and Dienes used the following equations:

where $K_1 = 84 \nu e^{S_{lv}^m/k} e^{-E_{lv}^m/kT}$

$$K_2 = 14 \nu e^{(S_{lv}^m + S_{2v}^b)/k} e^{-(E_{lv}^m + E_{2v}^b)/kT}$$

$$K_3 = \alpha \nu \lambda^2 e^{S_{lv}^m/k} e^{-E_{lv}^m/kT}$$

$$K_4 = \alpha \nu \lambda^2 e^{S_{2v}^m/k} e^{-E_{2v}^m/kT}$$

and α is the sink density and λ is the jump distance. The rate constants K_i vary with temperature and thereby give different shapes of annealing curves at different temperatures. Damask and Dienes have divided the temperature range into different regions. Their solutions show that whenever $K_1 > K_4$, $K_1 > K_2$ and $K_4 > K_3$, the divacancy concentration variation with time increases, passes thru a maximum and then decreases asymptotically to zero. Fig. 5 shows a plot of the rate constants versus temperature. For temperatures above 273°C and $\alpha \leq 10^{-14} \text{ cm}^{-2}$ the conditions for observing a maximum in the divacancy concentration on annealing are satisfied.

The damping peak height versus temperature which we observed is shown in Figs. 6-8 for annealing temperatures of 24°C and 40°C . These specimens were all quenched from temperatures close to the melting point in the well annealed condition. They clearly show a maximum in damping peak height at about 30 hours for annealing at 24°C and at about one hour for annealing at 40°C . The observed rapid decrease in time to reach a maximum with an increase in annealing temperature is also consistent with the computer calculations.

The process of equilibrating the vacancy-divacancy population in the absence of loss to sinks ($K_1 \gg K_4$) has been considered by deJong and Koehler (6) who obtained for the characteristic relaxation time of the process:

$$1/\tau = 7\lambda e^{-(E_{1v}^m + E_{2v}^b)/kT} (1 + 48 C_0 e^{E_{2v}^b/kT})^{1/2} \quad (10)$$

Figure 5

Logarithm of the rate constants versus reciprocal temperature.
The following values from Wang et al. (5) were used:

$$E_{1v}^m = 0.9 \text{ eV}$$

$$\nu_e S_{1v}^m / k = 4 \times 10^{13} \text{ sec.}^{-1}$$

$$E_{2v}^m = 0.66 \text{ eV}$$

$$E_{2v}^b = 0.4 \text{ eV}$$

$$\nu_e S_{2v}^m / k = 1.4 \times 10^{13} \text{ sec.}^{-1}$$

$$\lambda^2 = 10^{-15} \text{ cm.}^2$$

Figure 6

Divacancy damping peak height

$\delta_{\text{max}} - \delta_{\text{background}}$ versus annealing time.

$\circ$ Quenched from 1015°C into H₂O and annealed at 24°C.

Δ Water quenched from 1000°C and annealed at 24°C.

Frequency = 19.1 Hz.

Figure 7

Divacancy damping peak height

$\delta_{\text{max}} - \delta_{\text{background}}$ versus annealing time at 24°C after an air quench from 1000°C .

Frequency = 21.5 Hz.

Figure 8

Divacancy damping peak height $\delta_{\text{max}} - \delta_{\text{background}}$ versus annealing time at 40°C. The specimen was water quenched from 990°C.

Frequency = 17.0 Hz.

where τ is the time to form 88% of the final divacancy concentration and $C_o = C_{lv} + 2C_{2v}$. Fig. 9 shows values of τ for different binding energies using Eqn. (10) and $E_{lv}^m = 0.84 \text{ eV}$, $\nu = 6 \times 10^{12} \text{ sec.}^{-1}$, $C_o = 5 \times 10^{-4}$ and $T = 24^\circ\text{C}$ and 40°C . Figures 6-8 indicate that the time to reach equilibrium between single vacancies and divacancies is on the order of one hour at 40°C and 20 to 40 hours at 24°C . For these times Fig. 9 shows that Eqn. 10 predicts a binding energy of about 0.35eV from the 24°C data and about 0.30eV from the 40°C data. A lower binding would have shifted the maxima in the curves of Figures 6-8 to lower times. For a binding energy of about 0.1eV or less the time to reach equilibrium would have been on the order of 6 minutes or less for the 24°C anneals, and we should not have seen a maximum in the divacancy annealing curves. Our measurements of the time to reach a maximum in the annealing of divacancies therefore indicate a tightly bound pair of vacancies with a binding energy on the order of 0.3 to 0.35 eV.

Figure 9

The variation of the time to reach 88% of equilibrium between single and divacancies after a quench with the binding energy as determined from Eqn. 10. The total vacancy concentration at the quench temperature was taken to be 5×10^{-4} .

○ Equilibrium annealing temperature = 24° C.

□ Equilibrium annealing temperature = 40° C.

V. ANNEALING OF BACKGROUND DAMPING DUE TO DISLOCATION PINNING

The damping at temperatures other than those near the divacancy peak can be caused by instrumental causes, thermoelastic damping and dislocation motion. The instrumental damping level for the present apparatus has not been established but it is known to be less than 2×10^{-4} (the lowest damping value measured). Using the relations derived by Zener (29) the thermoelastic damping peak in 0.004 inch diameter gold wires occurs at about 10^5 Hz for temperatures of about 24°C . The thermoelastic damping at the temperatures and frequencies of our measurements can therefore be considered negligible. It then appears that background damping values in excess of about 10^{-4} are principally due to dislocation damping.

The dislocation internal friction in the amplitude independent strain amplitude range has been shown by Granato and Lücke (30) to be:

$$\delta = \Delta_D \frac{\omega \tau}{1 + \omega^2 \tau^2} \quad (11)$$

where $\Delta_D = 120 \Omega \lambda B L^4 / (\pi^3 C) \quad (11a)$

$$\tau = \tau_0 e^{E/kT}$$

L = distance between pinning points

B = a damping constant

ω = frequency

c = dislocation line tension

Ω = an orientation factor which takes into account the fact that the shear stress on the slip plane is less than the applied longitudinal stress

λ = dislocation density.

The above relation has been experimentally shown to describe the dislocation damping in the frequency range above about 20kHz (31, 32).

While Eqn. 11 predicts very low values of dislocation damping in the frequency range of the present experiments, many results have been reported which indicate that the dislocation damping is observed at low frequencies. Heiple and Birnbaum (32) measured the frequency dependence of the dislocation damping in copper and showed that below about 30 kHz the dislocation damping contribution was larger than that predicted by Eqn. 11. Routbort and Sack (33) have shown that in aluminum, copper and magnesium dislocation damping is observed down to frequencies of about 1Hz and that the dislocation contribution does not depend strongly on frequency at low frequencies. Our experiments also show a contribution to the background damping by dislocations as may be seen by comparing the damping values for slightly deformed specimens with those for the annealed specimens (Fig. 1). In the following discussion we will assume that the major contribution to the background is due to dislocations and that the functional dependence of the damping on the average loop length L given by Eqn. 11a applies at low frequencies. Eqn. 11a shows that the amplitude independent dislocation damping is proportional to the fourth power of the average dislocation loop length.

Granato, Hikata and Lücke (34) discussed the case where the number of pinning points arriving at the dislocations by diffusion varies as t^n where t = time. For defects whose dislocation interaction energy varies as the inverse radial distance from the dislocation $n = 2/3$, and after a time t the number of defects which have diffused to the dislocations, $c(t)$, will be given by the Cottrell-Bilby (35) relation:

$$c(t) \sim \left(\frac{ADt}{kT} \right)^{2/3} \quad (12)$$

where A is a parameter measuring the strength of the Cottrell interaction, and D is the pinning defect diffusion coefficient. As shown by Granato et al. (34) this leads to:

$$\delta_B = A_1 / [1 + \gamma c(t)]^4 \quad (13)$$

where A_1 and γ are material constants. Using Eqn. 12 this may be written as:

$$\delta_B = A_1 / [1 + \beta t^{2/3}]^4 \quad (14)$$

where β is a constant.

After a quench vacancies and divacancies will anneal to dislocations and stacking fault tetrahedra sinks. Since most of the vacancy type defects anneal at stacking fault tetrahedra, the dislocations will act as local sinks and those defects reaching the dislocations spend most of their lifetime diffusing in the volume of the crystal where the drift interaction leading to Eqn. 12 is significant. When the point

defects arrive at the dislocations they can act as pinning points either by forming jogs or by retaining their identity as point defects and interacting with the dislocations via their stress fields. In either case the concentration of vacancy type pinning points should be proportional to $c(t)$ as in Eqn. 12, and the pinning point density should vary as $t^{2/3}$. Agreement of the data with Eqn. 12 also implies that the dislocation pinning point interaction energy has an inverse distance dependence, $1/r$, as expected from an interaction between the dislocation stress field and the strain field around the pinning defect.

The changes of background damping on annealing after quenching from high temperatures was measured in the temperature range -110°C to $+24^{\circ}\text{C}$. The data which will be presented below is consistent with the changes in dislocation damping due to pinning by vacancy type defects discussed above. Immediately after a quench the background was of the order of 10^{-2} and on annealing a monotonic decrease in the background damping was observed. Fig. 10 shows the variation of the background dislocation damping, $\delta_B^{-1/4}$, with the annealing time, t , for annealing at 23°C . The damping was measured at -30°C and -100°C . We have assumed that $\beta t \gg 1$ in Eqn. 14. With this assumption the data are seen to exhibit a linear variation as expected from Eqns. 11a and 14. The decrease in damping on annealing at 23°C was greater for lower measuring temperatures as shown in Fig. 10.

The activation energy for diffusion of the pinning defects to the dislocations can be obtained by determining the temperature

dependence of the pinning rate as reflected by the decrease in background damping. The decrease in background damping was determined on aging at T_{A1} , and then the aging temperature was changed to T_{A2} , and the decrease in damping was further measured. The long range migration activation energy was then calculated by:

$$Q = \frac{3}{2} k \frac{T_{A1} T_{A2}}{T_{A1} - T_{A2}} \ln \left[\frac{d(\delta_B^{-1/4}) / d(t^{2/3}) \big|_{T_{A1}}}{d(\delta_B^{-1/4}) / d(t^{2/3}) \big|_{T_{A2}}} \right] \quad (15)$$

The data shown in Fig. 11 was obtained for a specimen annealed at 30°C and then at 38°C . The background damping was measured at -40°C . Analysis of the pinning rate data using Eqn. 15 results in an activation energy of $0.68 \pm 0.15\text{eV}$. This value for the long range diffusion activation energy of the pinning defects is in good agreement with the divacancy energy of motion determined from the frequency shift of the damping peak. The pinning defects which diffuse to the dislocations and pin them appear to be divacancies. The conclusion that E_{2v}^m (rotation) = E_{2v}^m (migration) implies that during annealing the divacancy lifetime is much greater than the single vacancy lifetime (6). This is consistent with a high divacancy binding energy and is in agreement with the result of the two analyses based on the divacancy relaxation measurements. Agreement of the pinning kinetics with the results calculated from a r^{-1} dependence of the dislocation-pinning point interaction energy suggests

Figure 10

The variation of background damping on annealing.

$\delta_B^{-1/4}$ is plotted vs. $t^{2/3}$.

Frequency = 19.2 Hz.

Quenching Temperature = 1040°C.

Annealing Temperature = 23°C.

⊙ = background damping at -30°C.

⊠ = background damping at -100°C.

Figure 11

The temperature dependence of the changes in background damping, $\delta_{OB}^{-1/4}$ measured at -40°C . is plotted vs. $t^{2/3}$ for aging at 30°C and 38°C .

□ 30°C anneal

○ 38°C anneal

Frequency = 17.0Hz

Quenching Temperature = 990°C .

that the dominant interaction of the divancies with the dislocation is a first order size effect rather than a modulus interaction.

The magnitude of the decrease of the background damping on annealing was observed to be about twice as large when the damping was measured at -100°C as when it was measured at -20°C . This suggests that the pinning point density was larger at lower temperatures for equal aging treatments. The data shown in Fig. 10 for damping measurements at -100°C and -30°C were taken on heating from low temperatures after each aging treatment, i. e. the -30°C data were taken shortly after the -100°C data. These temperatures were too low to allow divacancy motion in the lattice during the time of the experiment. The effect could have been caused by migration of defects along the dislocations until they come to a sink and disappear or meet another point defect to form a small cluster. Either case decreases the pinning point density and thereby increases the average dislocation loop length and the damping.

VI. CONCLUSIONS

An internal friction peak near 0°C for frequencies of about 9Hz in thin gold wires quenched from near the melting point was investigated. It is consistent with a divacancy rotating with an energy of motion of 0.65eV. The annealing of the divacancy damping peak indicates a binding energy of 0.3eV or greater. An analysis of the annealing of the background damping in terms of defects migrating to dislocations and pinning them yields a value of 0.68eV for the migration energy of the pinning defect. This suggests that the pinning defect is the divacancy.

APPENDIX

AN EXPERIMENTAL APPARATUS FOR MEASURING INTERNAL FRICTION IN THIN WIRES

An apparatus has been developed for measuring the damping of thin wires in the flexural mode of vibration as a function of temperature. It has the following features which are improvements over previous methods:

- a) a wide range of specimen diameters may be used. In particular the lower limit of the specimen diameter is limited only by the handling capabilities of the operator. Gold wires as small as 0.001 inch diameter have been used.
- b) the damping is measured in a stress free state.
- c) the frequency can be easily varied over a wide range from about 5Hz up to several hundred Hz.
- d) the specimens can be annealed (and/or heat treated) in-situ and no handling strains need be introduced.
- e) the apparatus is easily adapted to measurements over a wide temperature range.

A. Mechanical Design

The apparatus is shown in Figs. A-1 and A-2. The specimen (9) has the shape of a "U" and is suspended by two copper clamps (7) which are insulated from each other and from the aluminum chassis with teflon spacers (6). The specimen temperature is measured by a

thermocouple attached to the copper clamp (7). The horizontal portion of the sample is in the gap of a magnet (11) oriented so that the flux lines are parallel to the vertical portion of the specimen. The magnet may be either a permanent or an electro-magnet, and both have been used successfully. If the specimen is to be annealed or quenched in-situ by heating with an A.C. current, an electromagnet is generally used as it reduces the possibility of deflection of the specimen when the A.C. current is turned on. The frequency of the current used to heat the specimen is chosen to be far from the resonant frequency of the specimen to minimize its deflection during heating.

The specimen frequency is readily changed during an experiment by altering its length with the use of glass clamps (15) positioned to give the desired frequencies of vibration. The back glass slide is stationary and is mounted on a nylon guide (8). The front glass slide moves along the nylon guides to clamp the specimen against the back slide. The front glass slide is activated by a spring loaded plunger assembly (4) which is driven by a cam (2) whose position is determined by a 2/3 rpm motor. Several clamps can be used to change the specimen frequency sequentially and remotely.

The aluminum chassis is surrounded by an aluminum cylinder whose temperature is controlled by a resistance heater. The complete assembly is surrounded by a vacuum jacket and evacuated to less than 10^{-3} torr during the damping measurements. For temperatures in the range 77°K to 373°K the apparatus is immersed in a liquid nitrogen

Figure A-1

Experimental apparatus

1. Clamp drive rod.
2. Clamp drive cam.
3. Apparatus support rods.
4. Spring loaded clamp assembly.
5. Metal plate.
6. Teflon insulation.
7. Specimen clamps.
8. Holder for glass clamps.
9. Specimen.
10. Metal plate.
11. Magnet.
12. Plunger.
13. Plunger.
14. Spring.
15. Glass slides.

Figure A-2
Clamp assembly

(See Fig. A-1 for explanation of numbers.)

dewar. During high temperature heat treatment the specimen temperature can be monitored using an optical pyrometer or using the specimen resistivity.

B. Electrical Apparatus

Figure A-3 is a block diagram of the circuit for measuring the damping. The specimen is excited at its resonant frequency by using an oscillator tuned to the natural decay frequency of the specimen. The strain amplitude of oscillation was controlled by the current passed thru the specimen and could be as low as 10^{-7} . The damping was determined in free decay by switching the specimen leads from the oscillator to a high impedance amplifier using a make before break double-pole-double-throw switch arrangement. The oscillation of the specimen in the magnetic field generated a voltage which was amplified 10^4 times, passed thru a bandpass filter and fed into the amplitude discriminator shown in Fig. A-4. The amplitude discriminator passed the signal only when the amplitude was between two predetermined values. The signal was then sent to a counter which counts the number of cycles, N , for the signal to decay between two known amplitudes, A_2 and A_1 . Since the amplitude of the signal is proportional to the amplitude of the specimen motion in the magnetic field, the damping is:

$$\delta = 1/N \ln(A_2/A_1) .$$

Figure A-3

Electrical circuit for measuring damping.

Figure A-4

Amplitude discriminator

Engineered Electronics Logic Modules

T103 Flip-Flop

T105A One Shot

T106 Squaring Amplifier

T113 Triple Emitter Follower

T172 Voltage Comparator

T405 D. C. and Gate

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