but should be reasonably good for substitutional atoms and vacancies.

Bullough, R.: (comment) To get meaningful concentration distributions or kinetics in a calculation of this kind I believe it is most important to carefully consider the situation in and near the dislocation core. In particular I would suggest the use of a bounded interaction potential; that is bounded in the dislocation core such as that associated with a Peierls' dislocation. When solute atoms migrate to a dislocation there are two distinct possibilities: In the absence of chemical interaction between the solute atoms there is no need for a core boundary condition since no solute is lost from solution. If precipitation occurs on the dislocations then either the solute atoms are tightly bound to the dislocation or they cluster at various points along the dislocation line. In the former case $C=0$ or a finite transfer rate around the precipitate matrix interface is appropriate. In the latter case $C=C_g(t)$ at the core-matrix interface is appropriate where $C_g(t)$ is the core concentration, which is determined by the rate at which solute atoms are incorporated on to the nearest precipitate particles.

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Nucleation of Stacking Fault Tetrahedra in Gold

W. WESTDORP AND R. MADDIN

School of Metallurgical Engineering, University of Pennsylvania
Philadelphia 4, Pennsylvania, U.S.A.

Electron microscopic observations of the density and size of tetrahedra in quenche and annealed gold foils for two quenching temperatures (900°C, 980°C) each at one annealing temperature (100°C and 174°C) show an increase in the density of tetrahedra as a function of annealing time but no change in tetrahedra size with annealing time. Based upon these data, calculations are made to show that the nucleation of tetrahedra is the rate controlling step in their growth. The activation energy of the process is calculated as 1.22 ± 0.13 eV (T_Q=900°C, T_A=100°C) and 1.05 ± 0.13eV (T_Q=980°C, T_A=174°C).

1. Introduction

Supersaturated concentrations of vacancies can be trapped at room temperature by quenching thin wires or foils of face centered cubic metals from high temperatures. Electrical resistivity measurements have been used by Bauerle and Koehler[1] to detect their presence as well as the kinetics by which they anneal out. These annealing data have been interpreted by Kimura, Maddin and Kuhlmann-Wilsdorf[2] using a model by which some of the excess vacancies are annihilated at grain boundaries while the remaining aggregate to form clusters which on attaining critical size collapse to form prismatic loops as predicted by Kuhlmann-Wilsdorf[3]. In gold as well as some other metals (presumably those with low stacking fault energies), the prismatic loops transform into stacking fault tetrahedra as shown by transmission electron microscopy by Silcox and Hirsch.[4] Silcox and Hirsch correlated diffraction data to show that the faces of the tetrahedra were on {111} slip planes with stair rod dislocations along the six ⟨110⟩ edges.

Quenching from relatively low temperatures, *e.g.* Au<850°C, has been interpreted by Kimura *et al.*[2] to produce mainly single vacancies whereas quenching from higher temperatures produces a larger concentration of divacancies or larger clusters.

It has been assumed that annealing the quenched wires or foils causes the vacancies to aggregate into defect tetrahedra which

grow to their equilibrium size as determined by annealing temperature and time. It is also feasible that the nuclei of the defect tetrahedra are formed during the quench and grow during the annealing[2]. For example, Cotterill[5] in his thorough investigation of electrical resistivity of stacking-faults and lattice vacancies in gold assumed that negligible clustering occurs during quenching. Although Cotterill determined tetrahedron concentration and size distribution, these determinations were made mainly as a function of quenching temperature; hence no growth data are available.

In view of the uncertainty of nucleation events, it is considered necessary to determine tetrahedra density, size and growth on systematically varying quenching temperature, annealing temperature and annealing time.

2. Experimental Procedure

Gold wire (99.999%), one mm in diameter, was carefully rolled down to foils 0.01 cm thick and annealed for 72 hours at 900°C resulting in an average grain size of 10^{-2} cm. Specimen (1×0.5 cm) were quenched from a vertical tube furnace into iced brine. The specimens were mounted in an asbestos sandwich on a springloaded jig to obtain the fastest possible quench.

Within 2 min the specimens were transferred into liquid nitrogen or the annealing bath respectively. Annealed foils were polished down in a cyanide bath and observed in the electron microscope. The plates were analyzed as to tetrahedra density and size.

The method of counting tetrahedra was essentially that used by Cotterill[5] who shows that for specimens of grain size 10^{-2} cm, no correction is required for denudation around grain boundaries, dislocations or at the free surface. As with Cotterill the tetrahedra size and concentration are quite uniform. Hence large errors were not considered to be introduced because of loss of specimen in polishing.

3. Results

Quenching gold foil from <900°C followed by "immediate" electrothinning at sub-zero temperatures produces no visible tetrahedra or observable defects of any type. Tetrahedra do, however, develop on annealing the quenched gold foil.

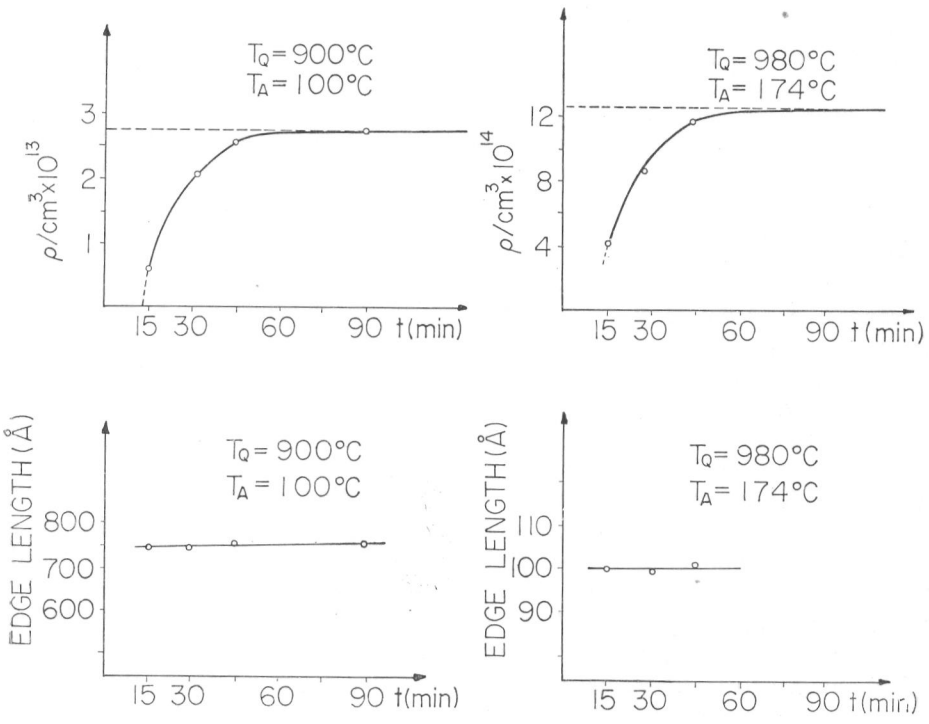

Fig. 1. Change of the density and size of tetrahedra with annealing time

The plot of the density of the tetrahedra *versus* the annealing time for two different quenching temperatures (see Fig. 1) shows clearly an increase in density with increasing annealing until a constant maximum value is established.

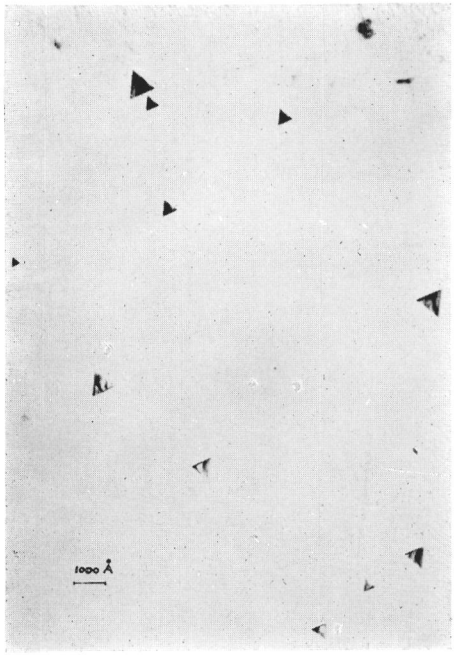

Fig. 2. Typical tetrahedra.
T_Q=900°C, T_A=100°C, t_A=15 min.

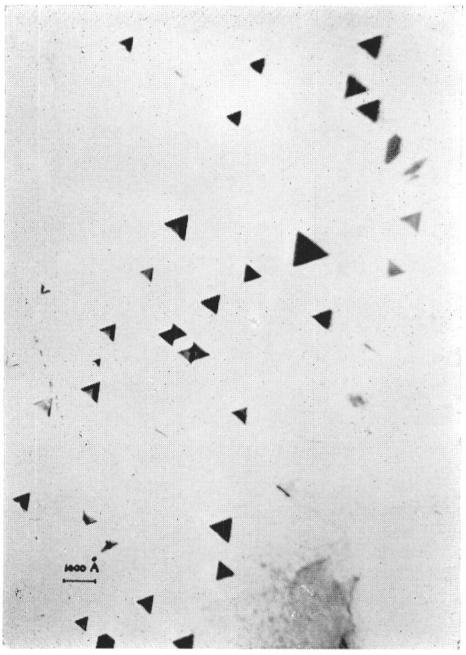

Fig. 3. Typical tetrahedra.
T_Q=900°C, T_A=100°C, t_A=45 min.

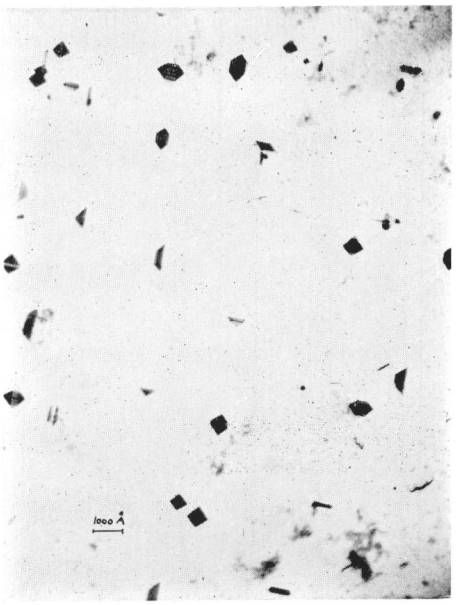

Fig. 4. Surface intersections of tetrahedra.
T_Q=900°C, T_A=100°C, t_A=45 min.

The average size of the tetrahedra was obtained from statistical analysis, the value for the average size being taken from measured Gaussian curves. Typical tetrahedra are shown in Figs. 2-4.

The plot of size of tetrahedra *versus* annealing time does not show a marked increase in size with annealing time, if any. Variation of tetrahedra size with different annealing temperatures for equal annealing time and quenching temperatures cannot be ruled out, however, and will be further investigated. This should give a final answer as to when the nucleation process takes place. If the nucleation of the tetrahedra occurs during the quench, the density of the tetrahedra should not change with increasing annealing temperature. If nucleation occurs during the anneal, we should expect to find a high concentration of small tetrahedra for high annealing temperatures and a low concentration of large tetrahedra for low annealing temperatures as our results show.

4. Discussion

The data so far observed show that the size of the tetrahedra remain constant with annealing time while the density increases, although the average size of the tetrahedra

increases with increasing annealing temperature. Based upon a tetrahedron edge length of 800 Å, we may make the following calculations: The number of vacancies per tetrahedron is 9.6×10^4. The radius of a sphere to be emptied of vacancies to form this tetrahedron is 1900 Å. On the other hand, the distance a vacancy will travel in the annealing time used in the experiments (of the order of 1000 sec) is 3 microns. Hence the distance travelled is large compared with the radius of the volume needed to supply the vacancies to form the defect (15 times). Furthermore, the time for vacancies to be emptied from a sphere of radius 1900 Å is only 3.5 seconds; far shorter than would be needed in order to observe the growth of tetrahedra considering that the foils must be electro-thinned. Growth at room temperature would occur in 4×10^4 sec, a time which lends itself to experimental confirmation.

It seems reasonable to conclude, therefore, that the rate controlling step in the formation of tetrahedra is their nucleation. It also seems reasonable to suggest that the nuclei are formed during the anneal, as suggested by Kuhlmann-Wilsdorf and Wilsdorf[6] rather than during the quench, since the time for growth is so small.

Finally we may calculate the activation energy for nucleation, Q, as follows: If the probability of the formation of a nucleus is, $p=(1-N_T/N_{TF})$ where N_T is the density of tetrahedra per cm^3 after an annealing time, t, at annealing temperature T (absolute) and N_{TF} is the total number of tetrahedra at saturation, then

$$\frac{d}{dt}\left(\frac{N_T}{N_{TF}}\right)=\left(1-\frac{N_T}{N_{TF}}\right)Ae^{-Q/kT}$$

where A is a rate constant, k the Boltzmann constant. Integrating,

$$N_T=N_{TF}[1-\exp\{A\ e^{-Q/kT}(t-t_0)\}]\ .$$

Q is then calculated from the slope of a plot of the logarithm of the exponent *versus* t. For a quenching temperature of 980°C and an annealing temperature of 174°C, Q is 1.05 ± 0.3 eV and 1.22 ± 0.3 eV for a quenching temperature 900°C and annealing temperature 100°C.

Acknowledgement

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DISCUSSION

Seeger, A.: In a recent study of the stability and metastability of stacking fault tetrahedra, Czjzek, myself, and Mader (Physica Status Solidi **2** (1962) 558) have concluded that stacking fault tetrahedra must be able to grow as such. I wonder whether from your investigation you have any comments on this.

Koehler, J. S.: Dr. M de Jong and I have attempted to describe the annealing kinetics of gold quenched from temperatures above 800°C. We agree with Professor Seeger in believing that rather small vacancy clusters occur as tetrahedra (six or more vacancies) and these tetrahedra grow. New growth steps are probably nucleated at the corners of the tetrahedra.

Maddin, R.: As pointed out in my lecture, our results indicate that tetrahedra as such did not grow at any appreciable rate. I should like to present two further arguments in support of this contention: (i) The fact that, in quenched noble metals, loops and tetrahedra may be observed simultaneously, proves that vacancy condensation can take place to cause non-equilibrium forms of dislocations (namely loops in this case). I should like to go further and claim that this is the rule rather than the exception. For example as was pointed out by Kuhlmann-Wilsdorf and Wilsdorf,

$\frac{1}{2}\langle 110\rangle$ quench loops in aluminum lie overwhelmingly on {111}, while {110} loops are rare, even though they are energetically much more favorable. Also the loops identified by Westmacott, Barnes and Smallman (lecture II A 8)* are definitely non-equilibrium forms. When the vacancy supersaturation has dropped to the extent that climb becomes slow, the frictional force on the original loops, the geometry of which was governed by dimb behavior ("vacancy precipitation", Berkeley Conference, 1961), drops and they then begin to assume equilibrium forms; by glide, by dissociation, and/or by conservative climb. This I am convinced, occurs in quenched gold, namely fast growth of dislocation loops which then transform into tetrahedra. (ii) Continuous tetrahedra growth and dissolution presumably involve the same stages only in reversed order. The high temperature required for the annealing out of tetrahedra compared to that for prismatic loops, indicates the existence of a high energy barrier. Such a barrier must inhibit tetrahedra growth at all temperatures much below that of tetrahedra annihilation.

* *Proc. Int. Conf. Cryst. Latt. Def. (1962)*: J. Phys. Soc. Japan **18** Suppl. III (1963) 50.

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On the Stability of Quenched Loops in Face-centered Cubic Metals

G. V. SAADA

IRSID 185 rue du President Roosevelt*
Saint Germain en Laye, (SO), France

The stability of quenched Frank sessile loops with respect to perfect prismatic loops is studied on a new model. It is concluded that measurement of the size of stacking fault rings does not give the right value for the stacking fault energy. The occurrence of stacking fault defects is predicted for metals with relatively high stacking fault energy like aluminum. Experiments to check the theory are proposed.

1. Introduction

Observations of thin films of quenched face-centered cubic metals have revealed several large defects[1]: perfect prismatic dislocation loops, Frank sessile loops surrounding a stacking fault, tetrahedra. Helical dislocations have been observed in alloys[2].

Although the existence, the geometrical features and some mechanisms by which they can transform into each other have been predicted or explained quite accurately[1),3)–7)], very little is known of the reasons for which a given defect is observed rather than another one.

Therefore, it is the purpose of this paper to study theoretically the stability of a Frank sessible loop with respect to a perfect prismatic loop by assuming they can transform into each other by a glide mechanism[7),8)].

The next paragraph of this paper will be devoted to the description of our model and of its general consequences. In the third paragraph we shall apply the results of our calculation to the description of the experimental situation in face-centered metals. We shall show that previous determinations of the stacking fault energies in the metals based upon the determination of the size of quenched loops are not reliable[9]. We shall compare our results to those obtained by

* On leave from October 1961 to September 1962 at Lawrence Radiation Laboratory, Inorganic Materials Research Division, University of California, Berkeley, California, U.S.A.