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Point Defects, and the Nature of Radiation Damage in F. C. C. Metals

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The recovery of electron bombarded gold and copper, and the relation to the migration energies of point defects is discussed. It is shown that the basic recovery spectrum of gold is very simple, consisting of a series of close interstitial-vacancy pair (Stage I), a background due to the migration of interstitials to nearby vacancies (Stage II), and the free migration of interstitials (Stage III, migration energy 0.71 eV). This interpretation agrees fully with quenching and cold-work data. In copper we have in addition close-pair substages and a free migration stage (I_E) due to recombination of metastable crowdions with vacancies. The concentration dependence of I_E is fully accounted for by this picture. An analysis of the experimental data indicates that in copper the threshold energy for crowdion formation is about 25 eV, whereas the absolute threshold (in <100>) is about 15 eV.

1. A Simple Model for Electron Radiation Damage in Metals, and its Relation to the Properties of Point Defects in Gold

The radiation damage in copper, even by electrons, is rather complicated (section 2). Since most experiments have been done on copper, the other f.c.c. metals were often considered in analogy to copper. We shall show in this paper that the electron radiation damage of gold is actually considerably simpler than that of copper and rather easily understood.

The simplest kind of radiation damage that we may expect in a pure metal after electron bombardment is as follows:

(1) Close interstitial-vacancy pairs. They are close to mechanical instability and will anneal out with first-order kinetics at very low temperatures.

(2) Interstitial-vacancy pairs which are further apart than those of (1), but still interact sufficiently with each other in order to lower appreciably the energy barrier for the migration of the more mobile partner, presumably the interstitial.

(3) Interstitials that are sufficiently far apart from the vacancies in order to be not influenced by them. They anneal out by random walks to sinks, mainly isolated vacancies.

(4) Isolated vacancies. The majority of these serve as sinks for interstitials. The remained anneal out either at dislocation sinks or by forming clusters.

The preceding picture agrees completely with the observations on the annealing of electron-bombarded gold[1], if (in the usual nomenclature) annealing stages I, II, etc. are identified with the annealing processes (1), (2), etc. given above (see Fig. 1).

Experiments on quenched and cold-worked gold are also in agreement with this assignment as we shall show presently. It appears now to be generally accepted that the energy of migration of single vacancies in gold is 0.83 eV and that it corresponds to Stage IV (and not to Stage III). Stage III after cold-work anneals out with an energy of migration of 0.71 ± 0.02 eV and essentially second-order kinetics, independent of the impurity content and the dislocation density[2),3)]. A corresponding well-defined activation energy cannot be found after quenching[2),3)]. Stage III after electron bombardment, however, gives the same activation energy, namely 0.72 ± 0.04 eV[4)].

By plastic deformation, vacancies and interstitials are produced in about the same concentrations[5)], spatially uncorrelated with each other. Very close Frenkel pairs are therefore exceedingly rare, and no Stage I is observed after low-temperature plastic deformation[6)]. Distant Frenkel pairs are more frequent and give rise to the quasi-continuous Stage II background shown as dashed line in Fig. 1. This stage is termi-

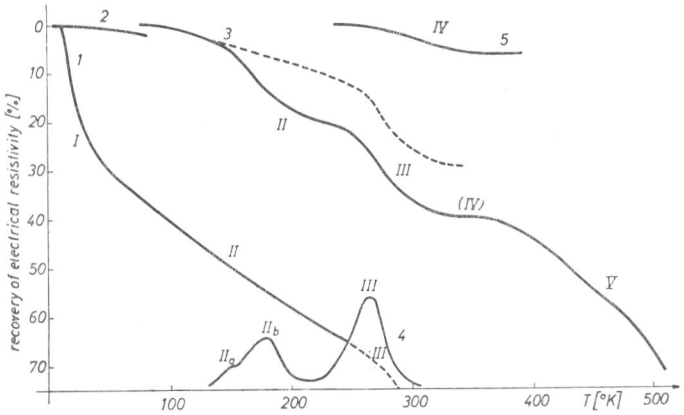

Fig. 1. Recovery Stages I-V in gold as observed after various treatments.
1: 2.5 MeV electron irradiation[1),4)], schematic
2: Cold-work at 4.2°K[6)]
3: Cold-work at 78°K[11)]
4: Stored-energy output during heating after cold-work at 78°K[7)], arbitrary units
5: Quenched from 1000°C[3)], resistivity given relative to that at 90°K.
The dashed part of curve 3 shows the presumable shape of the background recovery curve, *i. e.* without the substages in Stage II.

nated towards high temperatures by Stage III, the most pronounced stage in the point-defect recovery of cold-worked gold. According to the activation energy and the observed second-order kinetics[3)], it is to be attributed to the free migration of interstitials to vacancies, which are present in approximately equal concentrations. The capture cross-section for the vacancy-interstitial recombination is found to be of the correct order of magnitude[3)].

Superimposed on the recovery due to the migration of interstitials to vacancies two substages in Stage II are observed[7)]. The defects migrating in this temperature interval may also be responsible for the internal friction peaks observed in the range of Stage II by Hasiguti and Okuda[8),9)]. Up to now the defect migrating in the Stage II substages have not yet been identified. Both resistivity and internal friction experiments to investigate this problem are under way at Stuttgart. At present our suggestion is that the defect is a multiple vacancy, possibly interacting with impurities. Such a suggestion has been made earlier[10)]. Korevaar[11)] has raised objections against this view on the grounds that he did not find any measurable ordering in Stage II in a Au-7.5%Cu alloy that had been cold-worked at liquid nitrogen temperature. As will be shown elsewhere, due to the high density of sinks present in the form of other point defects one cannot expect much ordering from any point defect migrating at as low a temperature as that of Stage II. We consider therefore Korevaar's observations not to be a serious argument against our assignment.

Leaving aside the additional complications due to Stage II (which do not affect the interpretation of the electron bombardment data), the basic recovery spectrum of gold is thus exceedingly simple. It consists of a series of annealing substages corresponding to the annealing out of various interstitial-vacancy pairs. With increasing separation of the pairs the stages get closer and closer, forming a quasi-continuum, and leading up to the series limit of free interstitials migrating with an activation energy of 0.71 eV. In addition to nickel[12)–17)], gold is now the second f.c.c. metal in which the assignment of the annealing stages to defect migration energies was possible on the basis of arguments specific for the metal under consideration. In nickel it has been shown that Stage III is to be assigned to the migration of dumb-bell interstitials, and Stage IV to the migration of single vacancies. This agrees completely with the assignment given here for gold, if we assume that the interstitials

migrating in Stages II and III are dumb-bells. It appears likely that in all the noble metals the interstitials migrating in Stage III are in the dumb-bell configurations, although no direct proof for this has been given as yet. One of the internal friction peaks observed below room temperature in gold and copper by various workers might in fact be due to the rotation of the dumd-bells[13].

2. Radiation Damage in Copper

The analogy between gold and copper in the annealing of electron radiation damage is incomplete with respect to Stages I and II (see Fig. 2). Stages III and IV are similar in both cases, and the same interpretation should apply. The main differences between Cu and Au are as follows:

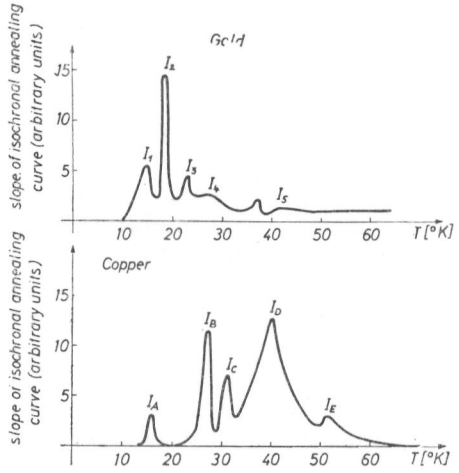

Fig. 2. Comparison of the fine structures of annealing Stage I after electron bombardment in gold[7] and copper[18]

(1) After electron bombardment, Stage II is more than an order of magnitude smaller in Cu than in Au.

(2) In Cu substage I_E is not a close pair stage but corresponds to a freely migrating defect.

(3) In Au there is no analogy for the large I_D substage.

(4) Under comparable conditions the number of resolved close-pair substages appears to be larger in gold than in copper. Similar differences exist in the annealing spectra of gold and copper after deuteron[19-21] and after fast neutron bombardment[22].

These differences can be explained in the following way [23]: Crowdions in copper are thought to be metastable [24], with a migration energy equal to that observed in stage I_E. If they did not anneal out in stage I_E, they would be converted at some higher temperature into the stable dumb-bell interstitial configuration. The threshold energy for the formation of crowdions in copper is between 25 eV and 30 eV. In gold the threshold energy for crowdion formation can be shown[23] to be so high that very few crowdions, if any at all, can have been formed in the experiments of Ward and Kauffman[1]. Since the ratio of ion radius to lattice parameter is considerably larger in gold than in copper, it may well be that the static crowdion is unstable in gold. If this is the case, a gold analogy to stage I_E could not even be detected after electron bombardment with higher energies or deuteron bombardment.

We arrive thus at the following picture for the radiation damage in copper. Two kinds of interstitials are formed, provided energies higher than 25 eV to 30 eV transferred into ⟨110⟩—directions, and provided that the dynamic crowdions propagating in these directions are not suddenly stopped by an obstacle such as a dislocation, a stacking-fault, or an impurity but rather come to rest gradually in a perfect crystal environment. Sudden stopping is thought to convert them into dumb-bells. Brinkman, Meechan, and Sosin[24] were indeed able to show that heavy cold-work prior to electron irradiation suppressed stage I_E (ascribed to crowdion migration) and enhanced stage III (dumb-bell migration).

The basic recovery spectrum of copper consists of two series of close-pair stages, one for the crowdions with a series limit at stage I_E, and one for the dumb-bells, with a series limit at stage III. The population of these two "line spectra" depends on the type of irradiation, the energies transferred to the copper atoms, the impurity content, and the dislocation density of the material. The dependence on the energy of the bombarding particles may be clearly seen in the experiments of Corbett and Walker[25] and Sosin[26]. The population of the substages (*e.g.* I_A) associated with close crowdion-vacancy pairs goes to zero with decreasing electron

energy long before the overall threshold energy is reached. As a matter of fact, the threshold for crowdion formation mentioned above was estimated in this way. The present picture accounts for the large stage II background annealing observed in some of the earlier irradiation damage work on copper and also for the existence of substages immediately above the I_E stage, as for example in the annealing after bombardment by a high dose of 1.4 MeV electrons[26].

Most of the features discussed here cannot be accounted for by the simple Walker-Seitz-Koehler model, which ascribes I_E to the three dimensional random walk of an interstitial and I_A to I_D to the corresponding close pair stages. This seems to have been realized by the Urbana group. They recently proposed to account for the difference between Cu and Au by assuming that the interstitials in gold are in the dumb-bell configuration and those in copper are in the octahedral position[27]. The latter assumption seems to be hard to reconcile with the theoretical result that the dumb-bell energy is at least one-half electron volt lower than the octahedral energy[28].

Against our interpretation of the low temperature annealing the following objection has been raised[29),30]. Corbett, Smith and Walker[31] have shown that the shift of the I_E-temperature with the defect concentration is compatible with a second order reaction, *i. e.* with an annealing rate proportional to the square of the defect concentration (not necessarily with bimolecular reaction kinetics). It has been argued that this is the law following from three-dimensional random walk but not from the migration of crowdions to an equal number of vacancy sinks. A detailed analysis (to be published elsewhere) shows, however, that the annealing rate for a concentration c of crowdions can be written as

$$dc/dt = -R(t) \exp(-E_m/kT)c^2 , \qquad (1)$$

where E_m is the migration energy of the crowdions, and $R(t)$ a function of time which depends on the spatial distribution of crowdions and vacancies. The law Eq. (1) is in very good agreement with the experiment. The annealing data on stage I_E can be fully understood in terms of the migration of crowdions. For further discussion of the properties of point defects see the contribution by W. Schüle to this conference.

3. Threshold Energies and Orientation Dependence of Damage Rate

The picture given in Section 2 for the electron radiation damage of copper could be tested very critically by experiments on single crystals. It predicts a strong orientation dependence of both the damage rate and the low temperature annealing substages. We have attempted to analyze the data available on the damage rate of polycrystalline copper in a preliminary way (using Sosin's[26] corrections for electron straggling and energy degradation and neglecting multiple damage production)[32]. We assumed that for any given crystallographic direction (Θ, φ) the threshold is sharp, characterized by an energy

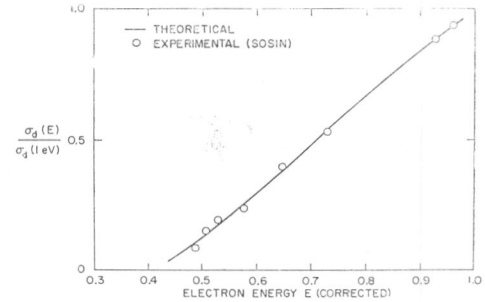

Fig. 3. Theoretical curve for the total cross-section for displacement σ_d as a function of electron energy E, fitted to the experimental points of Sosin[26]. The experimental points have been corrected for electron straggling and for energy degradation.

$T(\Theta, \varphi)$. T is expanded in cubic harmonics up to 6th degree, and the result is fitted to the results of Sosin[26] for the dependence of the damage rate on the electron energy. The fit shown in Fig. 3 is obtained for threshold energies $T_0 = 14.7$ eV in ⟨100⟩—directions, $T_1 = 30.6$ eV in ⟨110⟩—directions, and $T_2 = 70.3$ eV in ⟨111⟩—directions. The resistivity for a Frenkel pair comes out to be $\rho_F = 2.3\ \mu\Omega$ cm/% Frenkel pairs in rather good agreement with the value 2.5 $\mu\Omega$ cm/% Frenkel pairs, which has been derived from various annealing experiments[28),33]. These results mean that the absolute threshold for displacements in copper is about 15 eV. Due to the focussing in ⟨110⟩—directions the

threshold for crowdion production is somewhat lower than 30 eV, since T_1 corresponds to a saddle point of the T-surface and not to a relative minimum. This is in good agreement with the estimate of Section 2.

The orientation dependence of the damage rate predicted from such a model is quite marked. At low electron energies the damage rate is largest for bombardment in ⟨100⟩—directions. At energies around 0.6 MeV the theory predicts the largest damage rate for ⟨110⟩—directions, and at high electron energies for ⟨111⟩—directions.

It will be noted that our model agrees qualitatively, although not quantitatively, with the computer results of Gibson *et al.*[34] These authors also find that the threshold in ⟨100⟩—directions is smaller than in ⟨110⟩—directions, although not by as large an amount as we find. Our value $T_0=15$ eV does not appear unreasonably low in view of the observations of Dugdale[35], which suggest that in Cu_3Au copper atoms may be displaced with a threshold energy of about 10 eV.

Acknowledgments

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DISCUSSION

Vineyard, G. H.: I should like to express some scepticism about the existence of the crowdion in copper, even though Prof. Seeger's arguments are most ingenious. My points are the following:

a) The model of copper used in our calculations at Brookhaven definitely does not give a stable or a metastable crowdion. This is also true, I believe, of the calculations made by Brown and Johnson, and no calculation indicating crowdion stability has yet been reported.

b) If the crowdion and the split interstitial should both be stable the potential energy in configuration space would have to be complex indeed. For the crowdion is essentially a split interstitial in ⟨110⟩ orientation, and thus if the split interstitial is rotated the potential energy must have relative minima at the 12 different ⟨110⟩ directions as well as the 6 different ⟨100⟩ directions.

c) A strong argument which is usually offered for believing that the free interstitial cannot migrate in stage I (and therefore that free migration in stage I must involve another kind of interstitial) is that stage I recovery is not observed after cold work. However, there is another reason why stage I recovery should not be observed after cold work, namely, that interstitials formed in cold work must first be formed along closely spaced lines, and that these interstitials immediately cluster. Recent calculations at Brookhaven (see paper III A 1* of this conference) show that the di-interstitial is quite tightly bound, to the extent of about 0.6 eV in our model. This binding occurs for 3 of the 4 possible configurations of the di-interstitial and thus it is hard to imagine that a chain of interstitials could avoid it.

* *Proc. Int. Conf. Cryst. Latt. Def. (1962)*: J. Phys. Soc. Japan **18** Suppl. III (1963) 144.

Seeger, A.: I agree that no calculation leading to crowdion with stability in copper has yet been reported. However, the models mentioned by Vineyard are very simple and leave considerable room for further improvement. All the potential employed so far appear to be too hard in view of our result that the damage threshold may be as low as 15 eV. A softer potential would definitely form the metastability of the crowdion.

I also agree that the potential energy surface for interstitial have to be fairly complex in order to give us crowdion metastability. However, we must keep in mind that the complexity is already apparent in the experimental results. Compared with gold, we have in copper, so to speak, one defect too many that is capable of migrating over large distances.

Although I still think that the cold-work argument, used 8 years ago in order to support the essentials of the present interpretation, is a good one, our frame work would not at all be touched if the argument would no longer hold due to Vineyard's suggestion. I think there is now enough independent evidence to rule out the assignment of stage I_E to free three-dimensional interstitial migration. If Vineyard's mechanism for interstitial clustering in cold-worked metals were important, some indication for the break-up of these clusters should be found experimentally.

Koehler, J. S.: First, if we grant your calculation giving second order kinetics for crowdions we now have two possible mechanisms, crowdions and interstitials migrating in three dimensions so that one needs further experiments to decide which defect is responsible. Second, what is the experimental evidence which requires one to use interstitial migration to explain stage III? One could explain stage III in terms of divacancy migration, or to the break-up of interstitial clusters.

Seeger, A.: I agree that the stage I_E kinetics dose not distinguish between crowdion and interstitial migration. My point is that it cannot be claimed that the

experimental results rule out crowdion migration, as had been done in the literature.

Even if we leave aside the case of nickel, where we have fairly direct evidence for interstitial migration in stage III, I feel that the observed kinetics after electron bombardment and cold-work do not allow any simple explanation other than interstitial migration. *E.g.*, in gold we have analysed the kinetics quantitatively, and have found the right magnitude for interstitial-vacancy recombination cross-section. I do not think that these results could be explained by the break-up of interstitial clusters or by divacancy migration. None of these processes would give second-order kinetics. This has been concluded earlier by R. Walker, who had felt compelled to attribute stage III to vacancy migration. Of course, this possibility is now ruled out by the assignment of vacancy migration to stage IV.

Hasiguti, R. R.: It is almost certain that an interstitial is trapped by an impurity atom. Where do you assign the annealing of trapped interstitials?

Seeger, A.: For interstitial impurity interaction, I should like to refer to a paper by P. Simson and R. Sizmann: Z. Naturforschung **17a** (1962) 596. These authors show for nickel that in pure material stage III is large and stage IV very small, whereas the opposite is true for impure material. The interpretation is that in impure material the interstitials get trapped before they reach vacancy. Annihilation occurs by the migration of the vacancies. I believe that this explanation is true in general.

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The Interstitial Configurations in the Noble Metals

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The annealing spectrum observed in the region from 10 to 60°K in deuteron irradiated copper and silver are similar, that in silver being displaced towards lower temperatures. Recent experiments show that the annealing spectrum in electron irradiated gold is qualitatively different from that of copper and silver. It is therefore suggested that the interstitial which takes part in annealing in copper differs from that in gold. More specifically it is suggested that the interstitial is a cube centered interstitial in copper and a split (100) interstitial in gold. Reasons for this assignment and consequences of it are examined.

In spite of considerable experimental and theoretical work, the equilibrium configuration of the interstitial defect is not definitely established in the noble metals. Recent experiments by Ward and Kauffman[1] and by Bauer, de Ford, Kauffman and Koehler[2] have established that the annealing peak structure observed in gold is different from that found in copper and silver (see Magnuson, Palmer and Koehler[3], also Nilan and Granato[4] and Corbett, Smith and Walker[5]). This experimental information

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