American Society for Metals,
Philadelphia, Pa. Oct. 14, 1969

COO-1198-661

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9/16/69

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The Influence of Trace Impurities on Defect Behavior*

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Experiments which demonstrate that impurities nucleate clusters of interstitials and clusters of vacancies in gold are described. The experiments utilize specimens with total impurity concentration between 10^{-5} and 10^{-6} atom fraction. It is shown that the impurities influence damage production during electron irradiation at 80°K , alter annealing after quenching and after electron irradiation and influence the apparent activation energy observed in certain quenching and deformation experiments.

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* Research supported in part by the U. S. Atomic Energy Commission under Contract AT(11-1)-1198.

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Introduction

Recent research has shown that in many cases rather small impurity concentrations of impurities (of order 10^{-5}) can influence in an important way the annealing behavior of point defects. In the present paper an attempt will be made to discuss the various effects observed in face centered cubic metals.

We shall first consider gold since more research has been done on it than on any other metal. Then we consider aluminium and then silver and finally platinum. All other metals are very difficult to prepare and keep pure.

Gold. The first experiment which demonstrated the influence of small impurity concentrations on defect annealing was done by Ytterhus and Balluffi (1). They quenched gold from 700°C and annealed at 40°C . Figure 1 shows their results. The resistance ratio is a rough measure of total purity. A ratio of $3000 = \rho_{25^{\circ}\text{C}}/\rho_{4.2^{\circ}\text{K}}$ implies that $\rho_{4.2^{\circ}\text{K}} = 0.75 \times 10^{-9}$ ohm cm. For impurities which contribute 2×10^{-6} ohm cm per atomic percent impurity, this implies a total impurity concentration of 3.7×10^{-6} . Note the changes in the shape of the annealing curve as the purity increases.

R. Siegel (2) quenched gold from 900°C and 700°C and then annealed at 40°C . He found that the density and the size of the resulting vacancy tetrahedra depend on purity. His pictures are shown in Figures 2 and 3 and his numerical results are shown in Figures 4 and 5. Some impurity or impurity cluster serves as a nucleus for the vacancy tetrahedra. Siegel found that nickel and iron deliberately added do not introduce additional nuclei but copper acts as a nucleation center. Later Clarebrough and coworkers (3) showed that multivalent impurities will also nucleate tetrahedra.

Next Lee and Koehler (4) showed that the rate of damage production during 3 MEV electron irradiation at 120°K is sensitive to purity. Their data is shown in Figure 6. Additional information was obtained by Y. Shimomura (5) who took electron microscope pictures on gold after 3 MEV electron irradiation at 120°K . The specimens were thinned and examined at 2°C whereas stage III annealing occurs at about 40°C for the electron doses used. Shimomura saw interstitial precipitates (Figure 7). He found that the density of interstitial precipitates is larger in impure specimens. Moreover, the density does not increase with electron dose; the precipitates simply grow in size. Thus the interstitial precipitates are nucleated at an impurity or an impurity cluster. Shimomura's cluster density for two different purities are shown in Figure 8.

Lee and Koehler (4) also showed that the annealing of electron irradiated gold becomes simpler as the purity increases (Figure 8). First of all the amount of the continuous annealing at temperatures below stage III decreases as the purity increases and second, the amount of damage left after stage III annealing decreases with increasing purity. In gold strips having a measured resistivity at 4.2°K of 5×10^{-10} ohm cm, the resistivity remaining after annealing at 100°C for half an hour was less than 3% of the initial damage.

The gold and silver used were purchased from Cominco. Their analysis of two batches of gold and one batch of silver given in parts per million by weight were:

(a) Au							
Ca	Cu	Mg	Si	Ag	Ni		
0.1 ppm	0.1	0.1	0.3	0.1	2.1		

(b) Au					
Ca	Cu	Mg	Si	Ag	Fe
0.1	0.1	0.1	0.3	0.2	2.1

(c) Ag							
Al	Ca	Cr	Cu	Fe	Mg	Sr	V
0.1	0.2	0.3	0.3	0.5	0.2	0.3	5.0

If the resistivity at 4.2°K is used as a measure of the total impurity concentration, then if $\rho_{4.2^\circ K} < 2 \times 10^{-9}$ ohm cm, the size effect must be taken into account. For such high purity samples the electron mean free path is of the order of the specimen diameter. A further increase in purity will not change $\rho_{4.2^\circ K}$ much because most of the electron scattering occurs at the specimen surface. Figure 9 shows the relationship between the measured resistivity at 4.2°K and the resistivity of an infinitely large specimen of the same purity. Curves are given for strip 5 mils thick and wire 8 mils in diameter. It was assumed that diffuse scattering occurs at the specimen surface not specular reflection.

There is one other kind of experiment in which impurities play a role in the annealing of gold. If gold is rapidly quenched ($dT/dt \geq 4 \times 10^4$ °C/sec) from 700°C or if gold is deformed, or if gold is electron irradiated, then the annealing near room temperature shows an activation energy which is near the vacancy migration energy. However, the observed activation energy increases as the specimen purity increases. The data of Sharma, Lee and Koehler (6) is shown in Figure 10. We believe that the sink density is large in fast quenched gold as a result of the plastic deformation resulting from the rapid cooling. Moreover, we think that the sink density after a given quench depends on purity being higher in the higher purity specimen. This variation in sink density is associated with a variation in the effective migration energy observed. The ideas suggested above will require further experiments to clarify the situation.

Aluminum. In the case of aluminum, Lwin, Doyama and Koehler (7) have shown that the rate of damage production during electron irradiation at 120°K increases as the purity decreases. Also the amount annealing in stage II and the amount of resistivity remaining after stage III increase with increasing impurity content. The activation energy observed in stage III does not seem to depend much on purity. It is not known whether the single vacancy activation energy seen after quenching from low temperature is dependent on purity. It has been found (8) that large faulted dislocation loops are observed in 99.9999% pure aluminum quenched from 650°C to 0°C and annealed at 30°C. If 99.99% pure aluminum is quenched from 600°C to 0°C and annealed at 30°C, only unfaulted dislocation loops are seen. Thus in conclusion there are important impurity effects in aluminum but the data is not as complete as it is for gold.

Silver. In the case of silver and copper, research is complicated by the finite solubility of oxygen. Doyama and Koehler (9) and Cuddy and Machlin (10) quenched silver after annealing in an ultra high vacuum

(10^{-9} mm Hg) and filling the glass specimen container with spectroscopically pure helium. To date, no irradiation or deformation experiments have been done with comparable cleanliness.

Platinum. In the case of platinum, recent experiments by van den Beukel (11) and by G. Duesing and W. Schilling (12) have shown that an annealing stage at 300°K observed in deformed and in electron irradiated platinum is associated with some impurity effect. This stage was labeled stage III by earlier research workers. It is absent in very pure platinum. The stage at 250°C to 350°C is associated with an intrinsic annealing process. It should be labeled stage III. This high temperature stage is associated with vacancy migration.

The major point of this research is that both interstitial clusters and vacancy clusters are often nucleated at impurities or impurity clusters and that the annealing of point defects can be influenced by the cluster type and concentration. As additional experiments are done on other metals of high purity, we expect further cases to be added to the examples described here.

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Fig. 1. Annealing curves for gold specimens with various resistance ratios ($R_{24^\circ\text{C}}/R_{4.2^\circ\text{K}}$). All specimens were quenched from 700°C and annealed at 40°C .

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Fig. 2. Representative regions of three gold specimens, quenched from 700°C and annealed at 60°C as observed by electron microscopy.

(a) $\rho_{4.2^\circ\text{K}} = 2.34 \times 10^{-9} \text{ ohm cm}$

(b) $\rho_{4.2^\circ\text{K}} = 1.98 \times 10^{-9} \text{ ohm cm}$

(c) $\rho_{4.2^\circ\text{K}} = 1.26 \times 10^{-9} \text{ ohm cm}$

Fig. 3. Representative regions of three gold specimens, quenched from 900°C and annealed at 60°C as observed by electron microscopy.

- (a) $\rho_{4.2^\circ\text{K}} = 1.57 \times 10^{-9} \text{ ohm cm}$
- (b) $\rho_{4.2^\circ\text{K}} = 0.964 \times 10^{-9} \text{ ohm cm}$
- (c) $\rho_{4.2^\circ\text{K}} = 0.385 \times 10^{-9} \text{ ohm cm}$

Fig. 4. Vacancy precipitate density in gold as a function of the residual resistivity ($\rho_{4.2^\circ\text{K}}$) of the specimen for specimens quenched from 700°C and 900°C .

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Fig. 5. Final average vacancy precipitate size L_{rms} as a function of $\rho_{4.2^\circ K}$ for gold specimens quenched from 700°C and 900°C.

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Fig 5

Fig. 6. Damage production curves for gold upon 3 MEV electron irradiation at 120°K. ($\rho_{4.2^\circ\text{K}} = 0.380 \times 10^{-9}$ ohm cm for 8 mil wires, $\rho_{4.2^\circ\text{K}} = 0.141 \times 10^{-9}$ ohm cm for 5 mil thick strip; both these values are size corrected.)

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Fig. 7. High magnification pictures of defects observed before stage III annealing in gold irradiated at 130°K with 3 MEV electrons. Thinned at or below 3°C.

Fig. 8. Density of interstitial clusters versus integrated electron flux for gold irradiated with 3 MEV electrons at 130°K.

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Fig. 9. Size Correction for Resistivity. The measured resistivity at 4.2°K is plotted versus the resistivity that a sample of infinite size of the same purity would have at 4.2°K.

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Fig 9

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Fig. 10. Influence of purity on the apparent migration energy observed for vacancies in gold.