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^{57}Co Mössbauer study of the recovery process of electron-irradiated gold

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The recovery process of Au–10-at. ppm-Co alloy after electron irradiation at 78 K was investigated by means of ^{57}Co emission Mössbauer spectroscopy. Three satellite lines were observed and assigned to the small interstitial(I)–Co complexes, the micro-I-loops containing Co atoms and the divacancy-Co complexes, respectively. A fairly strong binding energy between the interstitial and Co atoms in small I-Co complexes, most probably larger than 0.2 eV, was deduced.

I. INTRODUCTION

Study on the interaction between point defects and foreign atoms is important for the fundamental understanding of diffusion related phenomena in metals and alloys. Although gold is one of the metals upon which research on this subject has been most widely performed, the atomistic and electronic mechanism of the interaction have not been clear. The hyperfine interaction study, especially by means of Mössbauer spectroscopy, is quite useful in this respect. Recently the authors performed ^{119}Sb Mössbauer study on very dilute Au-Sb alloy specimens quenched from high temperatures, and two kinds of vacancy associated states were detected.[1,2] On the other hand, in spite of some trials,[3,4] the defect-associated ^{57}Co atoms in Au have not been clearly identified until today. In the present study, it is our aim to clarify the ^{57}Co Mössbauer parameters of the defect-associated states in electron-irradiated, very-dilute Au-Co alloys.

In a previous study on the interaction between vacancies and solute atoms in Au using a precise electrical resistivity measurement and positron lifetime spectroscopy,[5] the authors found fairly strong binding energies ranging from 0.35 to 0.20 eV between vacancies and 3d transition element solutes, Fe, Co, and Ni. This was contrary to the obtained results of theoretical calculations so far, which predicted either repulsive or effectively no interaction. On the other hand, the interaction between self-interstitials and solute atoms in electron-irradiated Au alloys was systematically studied by Nakata *et al.*,[6,7] and it was found that undersized solute atoms such as Ni and Cu are fairly attractive to self-interstitials in Au. After electron irradiation, they found two substages of electrical resistivity decay in the stage-II recovery, both of which were attributed to the dissociation of small interstitial (I)–solute (S) complexes with two different sizes, IS and I_2S, as will be mentioned in detail later. In the present study, strong binding between Au interstitials and solute Co atoms was also expected, because the volume size of the Co atom in the Au matrix is -25.22% (Ref. 8), which is as small as those of Ni and Cu ($\Omega_{SF}=-21.92$ and $-27.81\ \%$) (Ref. 8) in Au.

II. EXPERIMENTAL PROCEDURES

The material we used was high purity Au (99.999%) 7 μm in thickness in which the main impurities detected by plasma-emission spectroscopy were Ca, Cu, Fe, and Mg with concentrations of 3, 1, 1, and 1 mass ppm, respectively. All specimens were annealed in helium gas at 1123 K for 0.6 ks, furnace cooled to 673 K, and quenched before the electron irradiation. The Mössbauer γ-ray source was prepared by electroplating 0.5 mCi (19 MBq) carrier-free ^{57}Co (containing <0.3 at. % ^{56}Co, <0.05 at. % ^{58}Co, and <0.002 at. % ^{60}Co) on a Au foil, using an electrolysis containing ^{57}Co in 0.1M HCl dilute solution and ammonium plus ammonium-citrate buffer solution with hydrazine hydrate.[9] After electroplating, in order to make a uniform solid solution and avoid the internal oxidation, the specimen was annealed in hydrogen gas flow for 14.4 ks at 1123 K. The Co concentration of the specimen made in this way was about 10 at. ppm.

^{57}Co Mössbauer measurements were performed by using the ^{57}Co source in the specimen and a Pd–2-at. %-Fe (enriched ^{57}Fe to 95.45%) absorber, 10 μm in thickness and kept at 291 K. The energy window was carefully chosen so as to minimize the superposition of Au L x rays on the 14.4 keV Mössbauer γ ray. Each spectrum was analyzed with the thin-foil approximation. The goodness of fit of the theoretical curve to the experimental data was estimated with the value of reduced χ^2, which was calculated over the whole velocity range of the experimental data. Electrical resistivity was measured by a standard dc four-probe method. Pulsed annealings of 180 s were made in baths of isopentane, acetone, water, and soybean oil at the temperatures 120–180, 200–280, 300–340, and >360 K, respectively. Both Mössbauer and resistivity measurements were performed between successive annealings at liquid-nitrogen temperature.

Irradiation was made with 28 MeV electrons to the total dose of $1\times10^{19} e/\text{cm}^2$ using the linear accelerator (LINAC) in The Research Reactor Institute, Kyoto University (KURRI). The specimen was kept in liquid nitrogen during irradiation, and it was never heated up before the measurement.

III. RESULTS AND DISCUSSION

Resistivity decays in isochronal annealing (180 s) of the electron-irradiated pure Au (99.999%) and two dilute Au-Co alloy specimens are shown in Fig. 1. It is widely accepted that radiation-produced self-interstitials (I) in Au are mobile even below 1 K.[10] Therefore, after irradiation at 78 K self-interstitials are supposed to be preserved only when they are trapped by solute atoms (S) and aggregate as I-S complexes. Since the radiation-induced resistivity is expected to increase as a result of the enhancement of the damage production rate by the presence of solute atoms, which have strong binding with self-interstitials, the resistivity increment will be a good measure for the magnitude of the interaction between I and S. Actually, in the present experiment, the radiation-induced resistivities of alloy specimens were about 4–5 times larger than that of pure Au, suggesting the strong binding between I and Co atoms.

The isochronal recovery process of three curves in Fig. 1 can be divided into two typical stages, i.e., stage II and stage III as shown in the figure. They can be interpreted as follows: Small I-S clusters grow large as I loops in stage II, and vacancies will migrate to be absorbed by I loops in stage III. On the other hand, a remarkable resistivity increase appears at around 550 K in the case of alloy specimens, as the lower two curves in Fig. 1 show. This could be caused by the resolution of small precipitates of Co atoms. In the present Mössbauer study, probably because the concentration of Co was very low, no change in spectrum due to this effect was observed.

Seven typical Mössbauer spectra obtained after irradiation at liquid-nitrogen temperature and after successive isochronal annealings by 180 s pulses at different temperatures between 120 and 320 K are shown in Fig. 2. The linewidth and the center shift of the spectra obtained by the least-squares fit by the single Lorentzian curve are plotted in Fig. 3. Although neither remarkable satellite lines nor changes in the center shifts were observed in all spectra, the linewidth showed a remarkable broadening by about 20% at the as-irradiated state and at around 240 K. The Mössbauer parameters of the main line, arising from the unperturbed Co atom, were obtained to be $\delta=0.77\pm0.01$ mm/s relative to the center of α-Fe and $\Gamma=0.26\pm0.01$ mm/s, where δ and Γ are the isomer shift and full width at half maximum (FWHM). This line will be called P_0. For the spectra between $T_A=140$ and 220 K, addition of a small doublet component gave the better fit in the analysis. The parameters of the new line, P_2, were obtained to be $\delta=0.76\pm0.02$ mm/s, $\Delta E_Q=0.17\pm0.02$ mm/s, and $\Gamma=0.26\pm0.02$ mm/s, where ΔE_Q is the magnitude of quadrupole splitting. This line must be caused by the trapping of interstitials by Co atoms. In the analysis of the data of the as-irradiated state, the presence of another extra doublet line, P_1, with the parameters $\delta=0.76\pm0.02$ mm/s, $\Delta E_Q=0.21\pm0.02$ mm/s, and $\Gamma=0.28\pm0.01$ mm/s, was found. In order to extract the contribution of this small component, the parameters of the P_0 and P_2 lines were kept fixed in the analysis. Two interpretations are possible for the line broadening of the P_1 line. One is due to the superposition of unresolved components. The other is diffusional effect due to the motion of probe atom in restricted geometry. In the latter case, the recoilless fraction of the corresponding line must be reduced significantly, similar to the case of the "cage motion" of ^{57}Co atoms in aluminum.[11] As a consequence, the total

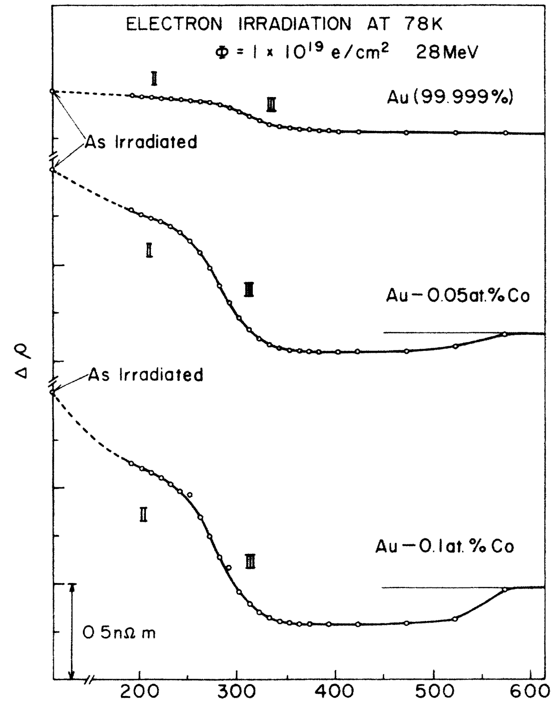

FIG. 1. Changes in resistivity on 180-s isochronal annealings of Au (99.999%) and two Au-Co dilute alloy specimens after electron irradiation at 78 K. Thin horizontal lines show the levels of electrical resistivity of alloy specimens after annealed at 1073 K and furnace cooled (full annealed state).

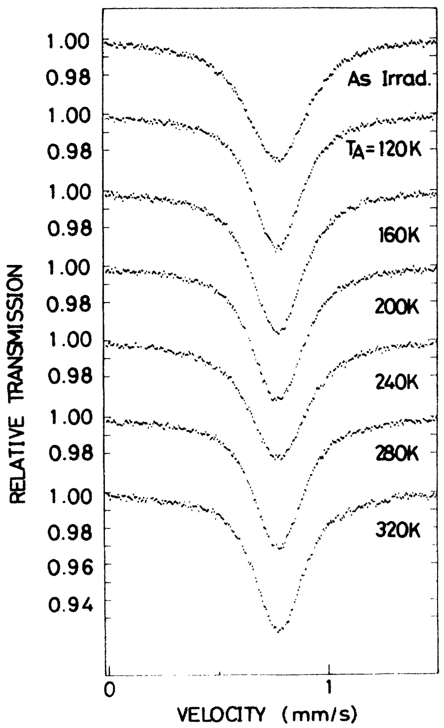

FIG. 2. Typical ^{57}Co emission Mössbauer spectra at 78 K obtained after electron irradiation at 78 K and on successive isochronal annealings by 180 s at the indicated temperatures. The velocity scale is relative to the center of α-Fe at 291 K.

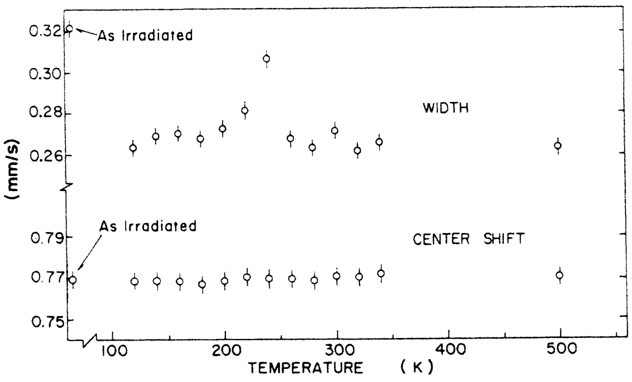

FIG. 3. The linewidth and the center shift of the spectra in Fig. 2 obtained by the least-squares fits to single Lorentzians and plotted as a function of annealing temperature.

resonance cross section of Mössbauer spectrum must be decreased appreciably. However, in our results the total area of Mössbauer absorption did not change, as can be seen in Fig. 2. Therefore, we interpret the broader width of the P_1 line as the superposition of unresolved components. The fitting procedure for the spectra of $T_A=240$ K are performed in the same way and the third component P_3 ($\delta=0.75\pm0.02$ mm/s, $\Delta E_Q=0.35\pm0.02$ mm/s, and $\Gamma=0.26\pm0.02$ mm/s) was extracted. Typical results of the least-squares fits to experimental data are presented in Fig. 4.

The fractional areas of the spectral components as the functions of the annealing temperature are shown in Fig. 5. By annealing at 120 K, the P_1 component disappeared and instead of it the unperturbed component P_0 increased. As mentioned before, interstitial atoms are trapped by solute atoms to form small *I*-*S* complexes during irradiation at 78 K. The P_1 line is, therefore, most probably assigned to the superposition of spectra arising from these small *I*-*S* complexes. On the other hand, the intensity of the P_2 component stayed constant in stage II and it gradually decreased in stage III. Therefore, the P_2 line is most likely assigned to Co atoms included in micro-*I*-loops.

According to Nakata *et al.*,[7] the small *I*-*S* complexes, such as I_1S and I_2S, dissociate in the early part of stage II as $I_1S \rightarrow I_1+S$ and $I_2S \rightarrow I_2+S$ in the case of Ni and Cu solutes in Au. Since the atomic size of the Co atom in Au is similar to that of Ni and Cu atoms, as mentioned before, the same reaction is expected for the Co solute. When this kinetic model is applied, the binding energy of I_1S or I_2S in the Au-Co alloy is estimated to range from 0.2 to 0.3 eV depending on the preexponential term of the dissociation rate. Another possible interpretation for the disappearance of the P_1 line at 120 K is due to the long-range migration of I_1S or I_2S complexes. As pointed out by Dederichs *et al.*,[12] when rotational and caging jumps of the mixed dumbbell occur subsequently, it can migrate in pairs without dissociation. In this case, the binding energy of these complexes should be larger than that obtained in the first model, because they are expected to be stable in their migration process. As a result, it can be concluded that the binding energy of these small *I*-*S* complexes is larger than 0.2 eV regardless of the models.

It is widely accepted that the most stable trapping configuration of an I_1S complex in Au with an undersized solute atom is a mixed dumbbell. For the I_2S complex, Nakata *et al.*[7] proposed the configuration of a mixed di-interstitials, that is, a mixed dumbbell combined with a self-dumbbell at its nearest-neighbor site. It is worthy of note that Co atoms are thought to occupy the dumbbell position in both I_1S and I_2S complexes. This is contrasted to the site of the Co atom in micro-*I*-loops,

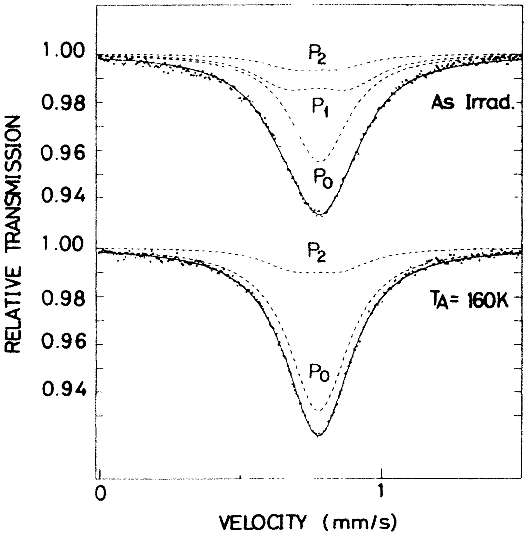

FIG. 4. Typical results of the least-squares fits to several Lorentzians. Solid curves are computer fits to the experimental spectra, and the dashed curves are resolved partial spectra.

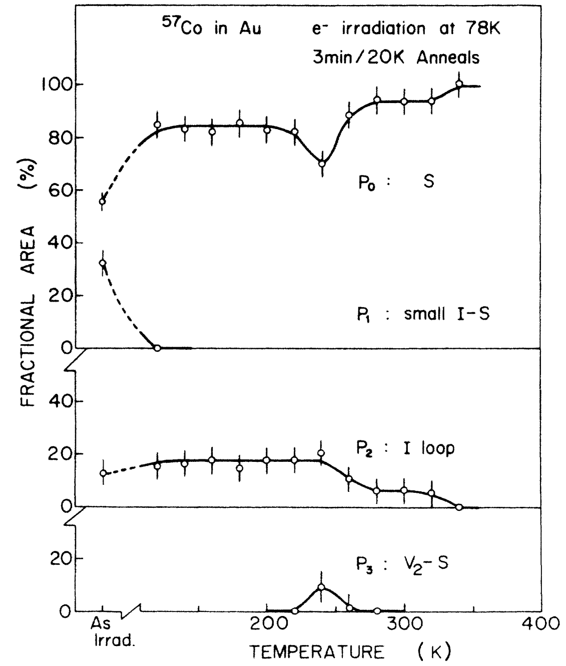

FIG. 5. The fractional areas of resolved spectral components P_0, P_1, P_2, and P_3 in Fig. 4 after isochronal annealings.

which would not be quite different from the normal substitutional site. The distinction in Mössbauer parameters in two lines, P_1 and P_2, must be due to such a difference in the positions of probe atoms.

Another new satellite line, which appeared near the onset temperature of stage III, P_3, can be assigned to the vacancy associated state. The trapping center acting at around 240 K was also detected by Deicher *et al.*[13] by means of $\gamma\gamma$ perturbed angular correlation (PAC) study. In the PAC study, the line which appeared at around 240 K was assigned to the trapping of Co atoms by monovacancies, since the electric field gradient of the association was found to be in the $\langle 110 \rangle$ direction. But the migration energy of the monovacancy deduced from their conclusion ranged from 0.62 to 0.72 eV,[13] which is about 0.1–0.2 eV lower than the value expected from the activation energy of self-diffusion, Q_0, measured at elevated temperatures. According to a simple vacancy mechanism of diffusion, Q_0 must be the sum of the formation energy and migration energy of the monovacancy.

On the basis of a large number of electrical resistivity studies on the recovery process of quenched-in vacancies, the migration energies and entropies of monovacancy (V_1) and divacancy (V_2) are well determined as $E_{V_1}^M = 0.85$ eV, $S_{V_1}^M = 1.5k$, and $E_{V_2}^M = 0.68$ eV, $S_{V_2}^M = 0.5k$,[14] where E^M, S^M, and k are migration energy, entropy, and Boltzmann constant. These values were also well confirmed by the positron lifetime study. Shirai *et al.*[14] succeeded in the quantitative interpretation of the isochronal annealing behavior of the positron lifetime spectrum in the quenched Au specimen by using the above values. The number of V_1 and V_2 associated with the Co atom during isochronal annealing in the present study can be estimated with the above values as well. Assuming that the frequency factor ν is 1×10^{13}, the geometrical factor g is 50 and initial concentrations of V_1 and V_2 are both 100 ppm, the number of V_1S and V_2S associations after isochronal annealing of 180 s/20 K from 120 to 240 K can be estimated from a theoretical calculation of rate equations as 1×10^{-3} and 1 ppm, respectively. Since the concentration of the latter is in good accordance with that of the P_3 line observed after annealed at 240 K in the present study, the P_3 line was assigned to the association of the divacancy with Co atoms in the present study. Although V_1 becomes mobile at around 280 K according to the above values and the binding energy between V_1 and the Co atom is as strong as 0.33 eV,[5] the appearance of V_1-Co association was not detected in the present study. This may arise from the fact that the Mössbauer parameters of single Co and V_1-Co association are very close to each other.

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