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Annealing of Cu_3Au irradiated with protons, α-particles and C ions at liquid nitrogen temperature

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Abstract

Isochronal annealing experiments have been performed from 120 to 460 K by electrical resistivity measurement on ordered and disordered Cu_3Au and Cu specimens irradiated below 85 K with protons, α and C ions of energies about 4–42 MeV. In the ordered Cu_3Au two large recovery stages centred around 290 and 380 K are observed, while in the disordered Cu_3Au a small stage centred around 150 K and three large stages centred around 190, 280 and 380 K are observed. In both ordered and disordered Cu_3Au, the 280–290-K- and 380-K-stages are interpreted to be due to the migration of free vacancies and the associated long-range ordering, and the migration of vacancies liberated from vacancy clusters and the associated ordering, respectively. The 150-K- and 190-K-stages in the disordered Cu_3Au are interpreted to be due to the migration of Cu and Au interstitials, respectively.

1. Introduction

Ordered alloys are most promising type of systems to study replacement collision in damage production processes and migration of vacancies, because their effects are observed as a large change in the ordered state. On the replacement collision in the ordered Cu_3Au, the irradiation experiments at low temperatures with fast neutrons [1,2] and high energy ions [3] demonstrated the number of replacements per Frenkel pair to be large, i.e., the order of several tens. From the electron microscopic observation of damage structures, the size distributions of disordered zones have been obtained [4–6].

For understanding of damage structures and behaviour of defects, annealing experiments in a wide temperature range are highly required, and the experiments on electron- and neutron-irradiated Cu_3Au have been made [1,2,7,8]. In a previous study we performed isochronal annealing experiments up to 90 K after irradiation below 30 K with high energy ions for both ordered and disordered Cu_3Au by electrical resistivity measurement [9]. In the ordered Cu_3Au the reverse annealing was observed in the α-particle-irradiated specimens but not in the proton-irradiated ones, probably due to the difference in the cascade damage structures produced by the two ion species. The structure of the annealing curves was different between the ordered and disordered Cu_3Au: It suggests that the long range migration of interstitials observed below 90 K in the ordered Cu_3Au is suppressed in the disordered one, reflecting the difference in the atomic arrangement between the two alloys. In the present study isochronal annealing experiments are extended up to 460 K for both ordered and disordered Cu_3Au irradiated with various ion species.

2. Experimental

The Cu_3Au specimens were 20–35 μm thick foil containing 25.8 at.% Au. Heat treatment for ordering and disordering is described in a previous paper [9]. The Cu specimens were 20–45 μm thick foil of 99.996% in purity. Irradiation was carried out below 85 K using liquid N_2 with protons, α-particles or C ions of various energies from 6 to 90 MeV obtained from a cyclotron of IPCR (RIKEN) under the condition for incident ions to penetrate the specimens. Isochronal annealing was made

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for 10 min periods, and electrical resistivities were measured at the liquid N_2 temperature. The irradiation conditions are listed in Table 1. The specimen cryostat was isolated from the vacuum system of a beam line by Al foil. The irradiation energies listed in Table 1 are those of outgoing ions from the Al foil.

3. Experimental results

Fig. 1ab and Fig. 2 show the results of isochronal annealing of the initially ordered Cu_3Au, initially disordered Cu_3Au and Cu, respectively. The resistivity increase $\Delta\rho$ is normalized to the initial resistivity increase $\Delta\rho_0$ in the as-irradiated state.

In the ordered specimens, two large recovery stages are evident in the temperature regions 240–340 and 340–460 K. In some case, at both stages the resistivity becomes lower than the value before irradiation, indicating the enhancement of long-range ordering. There seems to be a very small recovery stage around 160 K, but not evident. There is not so significant difference in annealing behaviour among irradiations with different ion species as observed in the previous annealing experiments up to 90 K [9].

In the disordered specimens three large recovery stages are observed in the temperature regions 160–220, 220–320 and 340–440 K, respectively. The latter two regions are approximately the same as those in the ordered specimens, but the recovery proceeds in the temperature region broader than that in the ordered specimen. It is to be noted that at the end of the second stage (280-K-stage), resistivity becomes lower than that before irradiation, i.e., ordering takes place. At higher temperatures (in the 380-K-stage) the resistivity still decreases approximately by 40% of $\Delta\rho_0$. In addition to these three stages, the recovery curves have an inflection around 150 K, indicating the presence of a recovery stage. However, wih increasing $\Delta\rho_0$, this stage gradually joins the first stage (190 K-stage). The inset of Fig. 1(b) shows the previously obtained result for a disordered specimen after irradiation below 15 K [9], indicating the commencement of a recovery stage around 80 K. Combined with the present result that the $\Delta\rho/\Delta\rho_0$ value around 110 K is already less than unity, it can be said that there exists a recovery stage between 80 and 110 K.

In Cu two recovery stages known as stage II and stage III are observed below 210 K and in the region of 220–320 K, respectively. However, their boundary is not so clear. There exists also a small recovery stage around 380 K, which is the same temperature region as in the ordered and disordered Cu_3Au.

Fig. 3 shows the isothermal annealing curves obtained for the ordered Cu_3Au at two temperatures in the stage centred around 290 K, i.e., 273 and 286 K. Although the irradiation energies and doses are different for both specimens, the apparent activation energy for the recovery process was roughly estimated to be 0.6–0.7 eV on the assumption of the first order kinetics.

4. Discussion

Combining the present results with our previous results on the isochronal annealing up to 90 K [9], the annealing curves in the temperature range from 18 to 440 K for the ordered and disordered Cu_3Au and Cu are qualitatively summarized as shown in Fig. 4. The

Table 1
List of specimens and properties

Specimen	Specimen no.	Irrad. Particle and energy (MeV)	$\langle E\rangle$ (MeV)	Dose (10^{15} particles/cm^2)	Initial resistivity ρ_0 (77 K) (μΩ cm)	Resistivity increase $\Delta\rho_0$ (77 K) (nΩ cm)
ord-Cu_3Au	1	p, 4.8	4.3	~8.4	2.9532	134.7
	2	p, 9.3	9.1	~28	2.5258	222.0
	3	α,18.0	14.9	~1.9	2.8184	131.5
	4	α,18.0	15.2	~2.7	2.3977	180.0
	5	α,18.8	16.0	~5.3	3.0339	392.5
	6	α,18.0	15.0	~3.8	3.0479	263.5
	7	c,56.7	33.1	~0.19	2.8976	477.6
dis-Cu_3Au	8	α,18.0	14.9	~1.9	10.0968	43.3
	9	α,20.5	17.7	~2.5	10.1252	53.9
	10	α,18.0	15.4	~3.4	9.9068	81.3
Cu	11	p, 4.8	3.8	~8.4	0.21922	13.1
	12	p, 9.3	8.6	~28	0.19935	13.1
	13	α,20.5	17.7	~2.5	0.19266	9.8
	14	α,18.0	15.1	~3.4	0.19999	14.8
	15	c,56.7	41.8	~0.19	0.19779	18.9

Included are the irradiation energy which is that of an outgoing beam from the cryostat window, and $\langle E\rangle$, the average energy of a beam in the specimen.

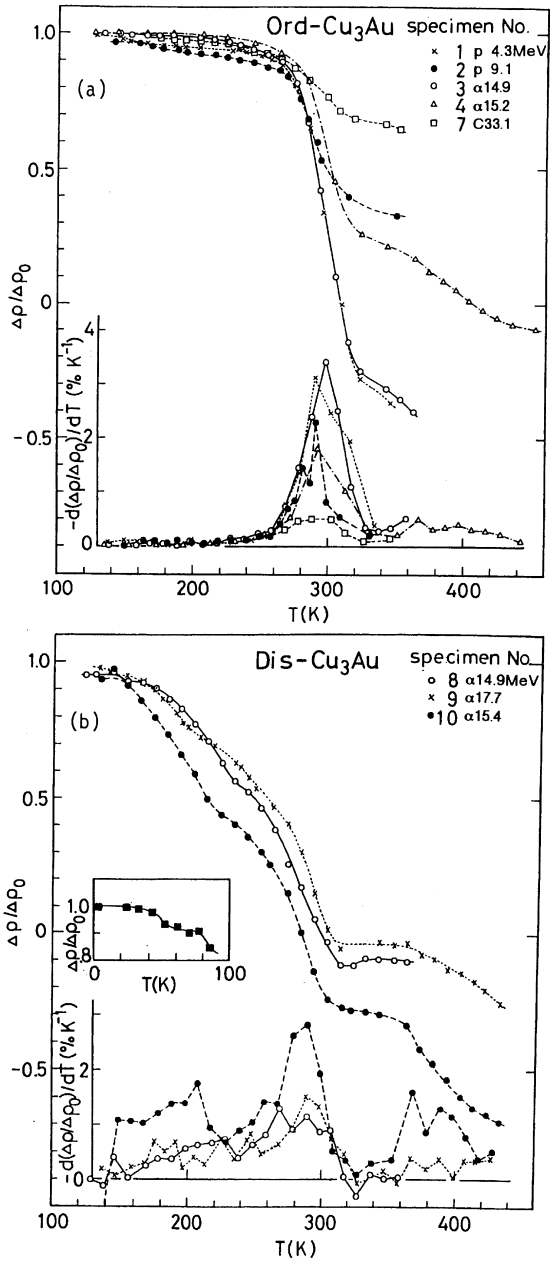

Fig. 1. Isochronal annealing curves of the electrical resistivity for 10 min periods and their derivatives for: (a) the ordered; (b) disordered Cu_3Au. The average beam energies in the specimens, $\langle E \rangle$, are indicated. The inset in (b) shows the previous result obtained after irradiation at 13.5 K with α-20.5 MeV ($\langle E \rangle = 17.5$ MeV).

observed recovery stages are listed in Table 2 together with the results hitherto reported by other authors [1,2,7,8]. These stages are labelled O-1–O-6 for the ordered Cu_3Au and D-1–D-6 for the disordered Cu_3Au in order of ascending temperature.

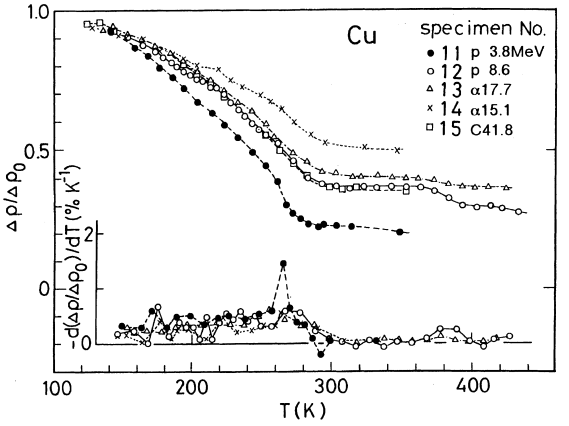

Fig. 2. Isochronal annealing curves of the electrical resistivity for 10 min periods and their derivatives for Cu.

4.1. Ordered Cu_3Au

In the annealing up to 90 K, two small recovery stages and a large stage were observed around 46, 52 and 75 K (stages O-1, O-2 and O-3), respectively [9]. Total amount of recovery below 90 K is approximately 20% of $\Delta\rho_0$. The $\Delta\rho_0$ is due to the formation of Frenkel pairs ($\Delta\rho_{0,FP}$) and due to the replacement between Cu and Au atoms. When the $\Delta\rho$ is renormalized to $\Delta\rho_{0,FP}$ in place of $\Delta\rho_0$, assuming that recovery in replacement does not take place below 90 K, 70–80% of $\Delta\rho_{0,FP}$ is recovered by annealing up to 90 K (Fig. 4(a)), which is of the same order of magnitude as the stage I recovery in Cu (Fig. 4 (c)) [9]. The stages O-1 and O-2 were interpreted to be due to the close pair recovery, and the stage O-3 due to the long-range migration of Cu interstitials, respectively [9].

At the two recovery stages O-5 and O-6, the enhancement of long-range ordering occurs. Such defect-enhanced ordering has been observed in the experiments

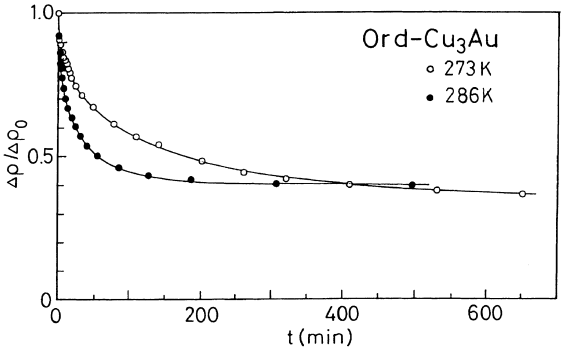

Fig. 3. Isothermal annealing curves at 273 (specimen No. 6, $\langle E \rangle = 15.0$ MeV) and 286 K (specimen No. 5, $\langle E \rangle = 16.0$ MeV) for the α-irradiated ordered Cu_3Au.

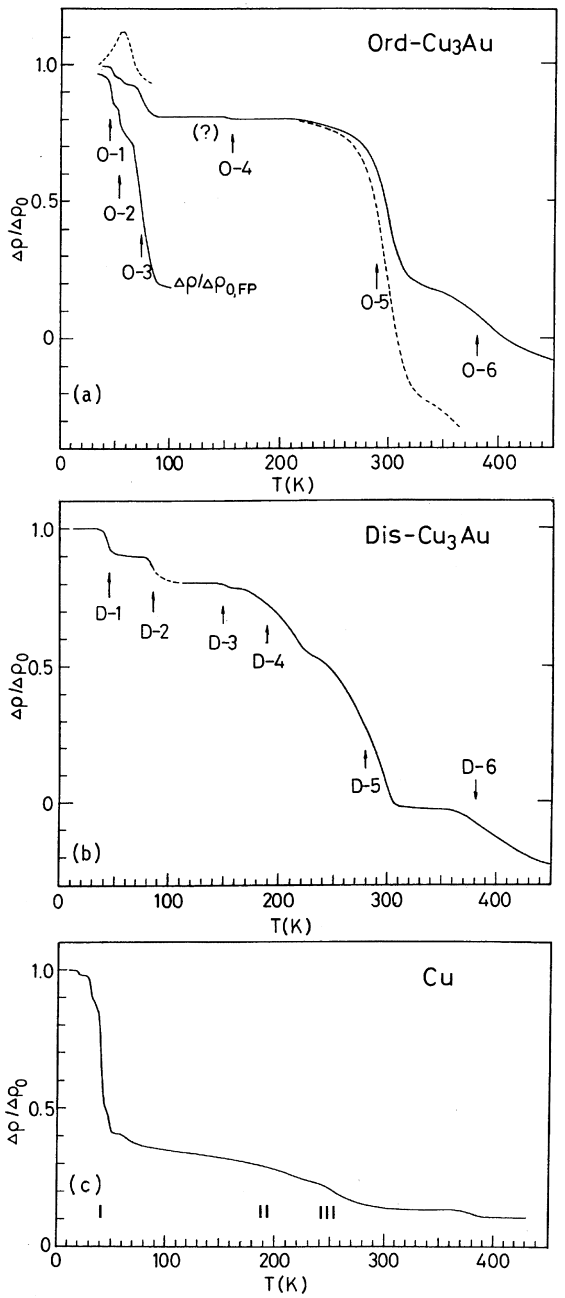

Fig. 4. Isochronal annealing curves qualitatively summarized by combining with the results previously obtained [9] for: (a) the ordered; (b) disordered Cu_3Au; (c) Cu. The curve renormalized to the resistivity increase due to the formation of Frenkel pairs, $\Delta\rho_{0,FP}$, and the reverse annealing observed below 90 K in the α-irradiated specimens in the previous work [9] are also indicated.

of quenching from temperatures above and also below T_C (the critical temperature for ordering) followed with annealing at temperatures below 473 K on the initially disordered or partially ordered Cu_3Au, and it has been demonstrated that migration of the quenched-in vacancies are responsible for this enhancement [10–12]. The effect of vacancies thermally formed during heating up unquenched specimens on the ordering appears above 473 K [10,12]. Therefore, the recovery in the stages O-5 and O-6 is considered to be related to the irradiation-introduced vacancies. According to the positron annihilation study on annealing of the ordered Cu_3Au irradiated with electrons at 20 K [13], the positron lifetime remains constant at 190 ps up to 220 K, and at 250 K a long lifetime component appears. It reaches maximum at 300–400 K, decreasing at higher temperatures towards the initial value. This result has been interpreted as follows: At 250 K vacancies start moving to form clusters, and in the region of 400–450 K they evaporate. On the basis of these results, the stages O-5 and O-6 can be considered to be the recovery due to migration of free vacancies to sinks and the recovery of long-range order associated with their migration to sinks or to form clusters, and the recovery due to migration of vacancies supplied as a result of evaporation of vacancy clusters and the associated ordering, respectively.

As seen from Fig. 1(a), despite a difference in the irradiation ion species, the specimens No. 1 and 3 with approximately same $\Delta\rho_0$ exhibit the same amounts of recovery at the stage O-5. Therefore, from Fig. 1(a) it can be said that the amount of recovery at the Stage O-5 is larger for smaller $\Delta\rho_0$. This behaviour can be understood on the basis of the assignment made above, because for smaller $\Delta\rho_0$ the concentration of vacancies is smaller, and, therefore, the vacancies make a larger number of jumps before annihilation at sinks or encountering other vacancies to form clusters, resulting in the larger recovery of long-range order. However, the interpretation of the stages O-5 and O-6 on the basis of the trapping of vacancies by impurities and detrapping from them could not be completely excluded.

The activation energy 0.6–0.7 eV for the stage O-5 recovery, which was obtained by a conventional analysis of isotherms, would not correspond to the migration energy of a vacancy, because at this stage not only annihilation of vacancies but also recovery of long-range order take place, and the contribution of the latter to the resistivity change is larger than that of the former [12].

4.2. Disordered Cu_3Au

In the ion irradiation six recovery stages from D-1 to D-6 were observed as in the isochronal annealing experiments for 40 min periods after electron irradiation below 20 K performed by Gilbert et al. [7]. Since the irradiation conditions and the annealing periods are different between these two experiments, the temperatures for stages would be slightly shifted, but it can be said that these six stages in both experiments correspond

Table 2
Recovery stages of ordered and disordered Cu_3Au

Specimen	Particle	Stage temperature (K)														
Ordered	n [1]						100							300		
Cu_3Au	n [2]	40		70									280			
	e^- (0.66 MeV) [8]	40		70										310		
	(2.36 MeV)	40		70					140					310		
	e^- (1.0 MeV) [7] (1.5 MeV)				75							240				410
	ions [9] +present	46	52		75					160 (?)			290		380	
Disordered	n [1]		Continuous													
Cu_3Au	n [2]										200		280			
	e^- (2.0 MeV) [8]		Continuous													
	e^- (1.0 MeV) [7]					90		130						330		410
	(1.5 MeV)		55			90		130			190			330		410
	Ions [9] +present	45			85				150		190		280		380	

The centre temperature of each stage is indicated.

well with each other. In the electron irradiation at 1.5 MeV, all six stages were observed, whereas at 1.0 MeV only four stages, i.e., the 90-K-, 130-K-, 330-K- and 410-K-stages, except for the 55-K- and 190-K-stages, were observed (Table 2). The displacement threshold energies for Cu and Au atoms were estimated to be 24 and 18 eV, respectively [14]. Considering that 1.5 MeV is sufficient to displace both Cu and Au atoms, but 1 MeV is insufficient and only Cu atoms are displaced, the 55-K- and 190-K-stages were ascribed to the recovery stages related to Au atomic defects.

As in the case of the ordered Cu_3Au, at the stage D-5 the recovery of long-range order is observed. Therefore, the stages D-5 and D-6 can also be ascribed to the recovery due to migration of free vacancies to sinks and the associated ordering, and the recovery due to migration of vacancies liberated from vacancy clusters and the associated ordering, respectively.

The irradiation energies in the present experiments are high enough to displace both Cu and Au atoms. From the comparison with the results of electron irradiation, it is considered that the stages D-1 and D-4 are related to Au atomic defects, and the stages D-2 and D-3 to Cu atomic defects. The step height at the inflection of the annealing curves around 150 K is very small. Judging from the derivatives of the curves, most parts of the temperature ranges of the stages D-3 And D-4 are overlapping. The total amount of recovery at both stages D-3 and D-4 is rather large, i.e., approximately 40%, which is of the same order of magnitude as that of the stage O-3 renormalized to $\Delta\rho_{0,FP}$ [9]. Therefore, the recovery stages D-3 and D-4 might be assigned to long-range migration of Cu- and Au-interstitials, respectively. The amounts of recovery at the stages D-1 and D-2 are small, approximately 10%, respectively. They might be ascribed to the close-pair recovery of Au-Frenkel pairs and to that of Cu-Frenkel pairs, respectively. The total recovery after annealing up to 220 K amounts to 50–60%, which is of the same order of magnitude as the stage I recovery in Cu and also the recovery up to 90 K renormalized to $\Delta\rho_{0,FP}$ in the ordered Cu_3Au.

In the disordered state there are large varieties of atomic configuration around interstitials and vacancies as compared with that in the ordered state, and, therefore, there might be a wide distribution in activation energies for migration. As a result, the temperature region of the recovery stage becomes broader in the disordered state than in the ordered state as observed in the experiment. The result that the vacancy migration takes place approximately in the same temperature range in the ordered and disordered states, but it is not the case for interstitials suggests that vacancies do not feel the difference in the atomic configurations around themselves between the two states so significant as interstitials do.

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