Kinetics of Pb₃Au Precipitation in Pb–Au Alloys

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The kinetics of precipitation in Pb-alloys containing 0.042–0.075 at% Au were followed by observing electrical resistivity change on isochronal or isothermal aging in a temperature range 195 to 488 K, after quenching from 488 K. With isothermal aging of Pb–0.042 at% Au alloy, the precipitation process basically differs in four temperature-ranges: (A) below 280 K; (B) 280–335 K; (C) 335–390 K; and (D) above 390 K. The resistivity increases in two distinct stages in range A, but in a single stage in range B. The activation energies are substantially the same for all of these stages: 44.4 ± 2.0 kJ/mol. In ranges C and D, the resistivity decreases in a single stage with different activation energies: 84.1 ± 1.5 kJ/mol for the range C, and 42.7 ± 2.0 kJ/mol for the range D. The kinetic laws are of second-order for both the ranges A and B; but of zero-order for the range C, and of first-order for the range D. The increase in resistivity is attributed to clustering (pre-precipitation) of solute atoms arising from recombination of Au interstitials. Metastable solubility curves of the clusters in lead are determined from the isothermal aging results. The decrease in resistivity is ascribed to Pb₃Au precipitation, the kinetics of which can be illustrated from a vacancy-turnover model (vacancy-catalyzed reaction). The two different activation energies for the Pb₃Au precipitation are assigned to migration energies of Au interstitial-vacancy pair and of Au interstitial, respectively. The binding energy between Au interstitial and vacancy is estimated to be 41.4 kJ/mol.

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I. Introduction

Solute gold atoms diffuse in solid lead primarily by a free interstitial mechanism at high temperatures of diffusion measurements⁽¹⁾⁽²⁾. It cannot be, however, ruled out that the gold interstitials interact attractively with lead lattice vacancies (interstitial-vacancy pair model for the diffusion)⁽³⁾⁽⁴⁾. Rossolimo *et al.*⁽⁵⁾ have shown that the precipitation of stable phase Pb₃Au from Pb–Au solid solutions is diffusion-controlled and that the activation energy (Q_p) for the precipitation is 87.1 kJ/mol in temperature range 333 to 403 K for Pb-alloys containing 0.05 to 0.1 at% Au, using electrical resistivity technique. This activation energy is about 2 times larger than that (Q_d) (41.8 kJ/mol) for diffusion at high temperatures. Kinetic results⁽⁶⁾ obtained by calorimetric technique have given a somewhat larger Q_p (100.3 kJ/mol) for aging of Pb–0.031 at% Au alloy in temperature range 348 to 373 K. More recently, resistivity measurements⁽⁷⁾ showed that the Q_p for 354–388 K increased from 43.4 to 80.1 kJ/mol with increasing Au-content from 0.01 to 0.05 at%. Since the precipitation is diffusion-limited, the Q_p may be connected with the state of solute in the diffusion responsible for the precipitation. Thus, the increase in Q_p (depression of precipitation rate) in the concentrated alloys was explained from a trapping of Au interstitial by self-association. It was however also suggested that the possibility

of trapping of Au by vacancies could not be eliminated. Even in high solute-concentration and low temperature ranges, the precipitation of interstitial solutes such as Ag^{(8)–(10)} and Ni⁽¹¹⁾ from lead occurred at rapid rate with small values of Q_p which are comparable to or less than Q_d , in contrast with the large Q_p for the Pb₃Au precipitation in these ranges.

The present paper reports the results of electrical resistivity measurements on kinetics of Au precipitation in a wide temperature range 195 to 488 K with Pb-alloys containing 0.042–0.075 at% Au, to study the solute state of Au responsible for the precipitation kinetics.

II. Experimental Procedure

Lead-gold alloys in the form of billet, 25 mm diameter and 50 mm length, were prepared from 99.999% lead and 99.99% gold in evacuated silica capsules, in the same manner as that used in studies on Pb–Ag alloys⁽⁸⁾. All the billets were homogenized for 360 ks at 488 K. Chemical analysis showed that the Au contents of the three billets used in this work were 0.042, 0.060 and 0.075 at%. Wire specimens of 1.7 mm diameter and 75 mm length were prepared by cold rolling and drawing the billets. Techniques of resistivity measurements were also as described in the earlier paper. During resistivity measurements, the specimens were dipped in liquid nitrogen of 77 K, at which none of supersaturated solid solution of Pb–Au alloys decomposes into the equilibrium phases⁽¹²⁾. A pure lead wire was used as a dummy. The resistivity of specimen was determined with a precision of better than 0.01%. The specimen was solution-annealed for 3.6 ks at 488 K under a vacuum of 1.3×10^{-2} Pa, and then quenched into iced water of 273 K. Immediately after quenching

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the specimen, its resistivity, ρ_0 , was determined. Subsequently the specimen was upquenched into a silicon oil bath of aging-temperature T_a and held there for a aging-time, t . The resistivity of the aged specimen, ρ , was expressed as ρ/ρ_0 . Two kinds of aging treatment were performed: (a) isochronal aging at $T_a=195$ – 488 K and (b) isothermal aging at $T_a=243$ – 443 K. The temperature of the aging bath was controlled within ± 0.1 K.

III. Experimental Results

1. Isochronal aging

Figure 1 shows the results of two isochronal aging experiments in which aging times were 40 s (curve (a)) and 360 s (curve (b)), respectively. A Pb-alloy containing 0.075 at% Au was used in this experiment. In the curve (a), the resistivity (ρ) increases clearly (but slightly) with increasing temperature (T_a) from 195 to 370 K (step 1), and then sharply decreases at T_a between 370 and 440 K (step 2). Subsequently, the ρ increases largely in the T_a range 440 to 476 K (step 3). The as-quenched resistivity ρ_0 is restored at 476 K which agrees closely with the solvus temperature of Pb₃Au determined by Rossolimo *et al.*⁽⁵⁾ Hence the steps (2) and (3) are attributed to precipitation of Pb₃Au from lead and its resolution into the matrix, respectively. The small increase of resistivity in the step (1) may be ascribed to a pre-precipitation process such as clustering observed in many Al-alloys⁽¹³⁾⁽¹⁴⁾ or a Pb–3.1 at% Mg alloy⁽¹⁵⁾. In the curve (b), the steps (2) and (3) occur in somewhat lower temperature range. The restoring temperature 476 K is however identical to that in curve (a), recognizing that the step (3) is due to the resolution of Pb₃Au into lead.

Fig. 1 Isochronal aging curves ((a) 40 s and (b) 360 s, at each temperature) of Pb–0.075 at% Au alloy, after quenching from 488 K.

2. Isothermal aging

Isotherms were examined by use of a Pb-alloy containing 0.042 at% Au. Figure 2 shows a curve obtained during aging at a low temperature ($T_a=313$ K). The resistivity increases at the start of the aging without any incubation period, reaches a maximum at aging time $t=t_m^I$ and remains roughly constant up to t_s' . After the t_s' , the resistivity decreases and ends its decay at t_f . The effect of T_a on the resistivity-increase process is indicated in Fig. 3 which shows solely the initial stage of isotherms at T_a between 280 and 335 K (range B). The maximum resistivity (ρ_m^I) attained at t_m^I is roughly independent of T_a . Figure 4 shows that the resistivity increases in two successive stages at T_a below 280 K (range A): After reaching the maximum at the t_m^I , the resistivity begins promptly an additional increase and then attains a second maximum (ρ_m^{II}) at t_m^{II} . After reaching the ρ_m^{II} , the ρ instantly decreases

Fig. 2 Isothermal aging curve of Pb–0.042 at% Au alloy at 313 K, after quenching from 488 K.

Fig. 3 The initial parts of isotherms at T_a of 280–335 K (range B), showing solely increase in resistivity: The same alloy as in Fig. 2.

Fig. 4 The first and second stages of resistivity increase during aging at T_a below 280 K (range A). Here, the initial part of the first stage in resistivity increase is not shown for simplicity: The same alloy as in Fig. 2.

exhibiting a resistivity peak at t_m^{II} . The ρ_m^{II} is also roughly independent of T_a . Figure 5 shows isotherms at T_a between 335 and 390 K (range C). The ρ decreases in a single stage with time and ends its decay at t_f . The final resistivity (ρ_f) attained by ρ at t_f is about $0.975\rho_0$ and roughly independent of T_a . There is no indication of any increase in resistivity. Isotherms at T_a above 390 K (range

D) are shown in Fig. 6. The ρ decreases again in a single stage, but the value of ρ_f increases with increasing T_a . This dependence of the ρ_f on T_a can be verified by the solubility curve of Pb_3Au reported by Rossolimo *et al.*⁽⁵⁾, which shows a rapid increase of Pb_3Au solubility into lead with increasing temperature above 400 K.

Fig. 5 Isothermal aging curves at T_a of 335–390 K (range C): The same alloy as in Fig. 2.

Fig. 6 Isothermal aging curves at T_a above 390 K (range D): The same alloy as in Fig. 2.

Fig. 7 Remaining fractional increase in resistivity as a function of aging time at T_a of 280–335 K. The results were obtained from the curves of Fig. 3: Test of second-order reaction.

3. Kinetic Law

(1) Stages of resistivity increase

The remaining fractional increase $(1-f)$ in resistivity at a given time t is found from Fig. 3 with an equation, $(1-f) = \Delta\rho^I / \Delta\rho_m^I = (\rho_m^I - \rho) / (\rho_m^I - \rho_0)$, for the whole of resistivity-increase stage at the T_a between 280 and 335 K (range B). Figure 7 shows the course of $1/(1-f)$ plotted against t for these T_a . The result indicates that the initial part ($(1-f) > 0.15$) of this stage obeys a quadratic kinetics. Figure 4 gives $(1-f)$ for the T_a below 280 K (range A): For the first stage of resistivity increase, with

the same equation as that described above; and for the second stage, with an equation, $\Delta\rho^{II} / \Delta\rho_m^{II} = (\rho_m^{II} - \rho) / (\rho_m^{II} - \rho_m^I)$. These two stages were also of second-order kinetics (not shown).

(2) Stages of resistivity decrease

Figures 5 and 6 give the remaining fractional decrease $(1-f)$ in resistivity with an equation, $(1-f) = \Delta\rho / \Delta\rho_f = (\rho - \rho_f) / (\rho_0 - \rho_f)$, for the whole of resistivity-decrease stages at the T_a between 335 and 390 K (range C; Fig. 5) and above 390 K (range D; Fig. 6). In Fig. 8, (a) and (b) respectively show the courses of $\log(1-f)$ and of $(1-f)$ plotted against t at the T_a in range C. This precipitation

Fig. 8 Remaining fractional decrease in resistivity as a function of aging time at T_a of 335–390 K. The results were obtained from the curves of Fig. 5: (a) Test of first-order reaction. (b) Test of zero-order reaction.

stage obeys a zero-order kinetics rather than first-order, but possibly a first-order kinetics in the later stage ($(1-f) < 0.1$). Figure 9 shows the $\log(1-f)$ -versus- t relation for aging at the T_a in range D. The results indicate that this stage is of a first-order and differs in kinetics from that in range C.

4. Activation energy

The activation energy (Q_p) for precipitation in the different T_a -ranges described above was evaluated from the temperature dependence of characteristic times for the precipitations. Figure 10 shows Arrhenius plots of t_m^I and t_m^{II} for the T_a below 335 K (ranges A and B). These plots give substantially the same Q_p , 44.4 ± 2.0 kJ/mol, for all of the three stages (the first and second stages of resistivity increase). This Q_p is close to the activation energy Q_d (41.8 kJ/mol) which was determined from diffusion experiments at high temperatures of solid solutions and assigned to migration energy of interstitial Au singlet⁽¹⁾⁽²⁾. Figure 11 shows Arrhenius plots of $t_{0.5}$ for the T_a between 335 and 390 K (range C) where the resistivity merely decreases. Here, $t_{0.5}$ is the time to complete one-half the total decrease in resistivity. These plots yield somewhat higher value of Q_p , 84.1 ± 1.5 kJ/mol, which is in good agreement with 87.1 and 80.1 kJ/mol reported by Rossolimo *et al.*⁽⁵⁾ and Campbell *et al.*⁽⁷⁾ for precipitation in the corresponding temperature and Au-concentration ranges. Figure 12 shows Arrhenius plots of relaxation time (τ) for precipitation at the T_a above 390 K (range D). Since the relaxation time of first-order reaction is independent of the initial concentration of the reactants, these plots are capable of yielding the Q_p , although the ρ_i depends on T_a in this temperature range. The Q_p , 42.7 ± 2.0 kJ/mol, estimated from Fig. 12 is certainly lower than that for the T_a -range C (335–390 K).

Table 1 summarizes the kinetic results obtained from the present experiments on the pre-precipitation (clustering) and Pb_3Au precipitation in the Pb-alloy containing 0.042 at% Au.

Fig. 9 Remaining fractional decrease in resistivity as a function of aging time at T_a above 390 K. The results were obtained from the curves of Fig. 6: Test of first-order reaction.

Fig. 10 Temperature dependences of times t_m^I and t_m^{II} to reach, respectively, the first and second maximum of resistivity increase at T_a below 335 K: Pb-0.042 at% Au alloy.

Fig. 11 Temperature dependence of half-time ($t_{0.5}$) for resistivity decrease at T_a of 335–390 K: Pb–0.042 at% Au alloy.

Fig. 12 Temperature dependence of relaxation time (τ) obtained from resistivity decrease at T_a above 390 K: Pb–0.042 at% Au alloy.

5. Concentration dependence of characteristic temperatures

Figure 13 shows the relations between T_a and amounts of the maximum increase in resistivity, i.e. $(\rho_m's/\rho_0) - 1.000$, for the Pb–0.042 at% Au alloy. There exist two characteristic temperatures— $T_c(1)$ and $T_c(2)$, where $T_c(1) > T_c(2)$: No increase in resistivity occurs during isothermal aging at T_a above the $T_c(1)$. The resistivity increases in a single stage at T_a between the $T_c(1)$ and the $T_c(2)$, but in two stages at T_a below the $T_c(2)$. A value of 335 ± 5 K was taken as the $T_c(1)$, and 280 ± 5 K as the $T_c(2)$ for this alloy. Figure 14 shows the Au-concentration dependence of $T_c(1)$ by curve (a), and that of $T_c(2)$ by curve (b).

Table 1 Order of reaction, n -th, and activation energy, Q_p , for pre-precipitation (resistivity increase) and precipitation (resistivity decrease) at T_a in four different temperature-ranges, A, B, C and D: Pb–0.042 at% Au alloy.

T_a / K	T_a range	Resistivity change	n -th	Q_p / kJ · mol ⁻¹
below 280	A	increase	2	43.7 ± 2.0
		increase	2	45.0 ± 2.0
280–335	B	increase	2	44.4 ± 1.5
335–390	C	decrease	0 ($f < 0.9$)*	84.1 ± 1.5
			1 ($f > 0.9$)	
above 390	D	decrease	1	42.7 ± 2.0

* f is the precipitation fraction.

Fig. 13 Relations between T_a and amounts of maximum increase in resistivity, i.e. $(\rho_m's/\rho_0) - 1.000$, for Pb–0.042 at% Au alloy.

Fig. 14 Metastable solvus lines ((a) and (b)) in Pb–Au system. Curve A: Pb₃Au solvus determined by Rossolimo *et al.* (1973).

IV. Discussion

The results shown in Figs. 1–4 suggest that the free Au-interstitial can be frozen-in within the solid solution by quenching the alloys from 488 K to iced water.

1. Pre-precipitation

The decomposition of the super-saturated solution occurs firstly with increase in resistivity during aging at low temperatures below $T_c(1)$ (ranges A and B). It is often assumed that during clustering of solutes the resistivity reaches a maximum at the same cluster-size regardless of aging temperature⁽¹³⁾. Hence the activation energy for the clustering is deduced from the time to reach the maximum at the each aging temperature. Most theories^{(16)–(18)} indicate that the resistivity increase is really due to the clustering (pre-precipitation), apart from the discrepancy between the theories and experiments concerning the critical size of the clusters associated with the resistivity maximum. Figure 13 indicates three features of amounts of the maximum increase in resistivity for the Pb–Au alloys: (1) These amounts are roughly independent of T_a within a given T_a -range below 280 K (range A) (or 280–335 K (range B)), with 0.042 at% Au alloy. This result suggests that the number of clusters does not differ from one T_a to another in a given T_a -range, because this number may be fixed immediately after quenching the alloys and not controlled by the aging temperature. Contrary to this, in Al–Zn alloys⁽¹³⁾ the number of clusters is controlled by aging temperatures. (2) These amounts are much small, that is about 0.25% of ρ_0 with ρ_m^I and 0.50% with ρ_m^{II} , which are one order smaller than that reported for clustering in Al-base alloys⁽¹³⁾⁽¹⁴⁾ or a Pb–Mg alloy⁽¹⁵⁾. This result may be due to the small number of clusters formed in the Pb–Au alloy, since the concentration of the solute is one order lower in this alloy than in the other clustering-type alloys. (3) This amount with ρ_m^{II} is 2 times larger than that with ρ_m^I . This elevation of the maximum resistivity is possibly due to an increase in electron-scattering effectiveness of the clusters and hence a change in nature of the clusters—for instance, structure and composition, since the number of clusters may be fixed immediately after quenching. Thus two types of cluster, $C_s(1)$ and $C_s(2)$, may form in two different T_a -ranges A and B. The thermal stability of the clusters is higher for the $C_s(1)$ than for the $C_s(2)$. In Fig. 14, the curve (a) shows Auconcentration dependence of the thermal stability (metastable solvus) for the $C_s(1)$; and the curve (b), for the $C_s(2)$. The nature of the clusters, however, is not clear at present.

The clusterings (pre-precipitations) obey the kinetic law of second-order and proceed with the activation energy (Q_p) 44.4 kJ/mol, which may be reasonable as energy of motion of free interstitials. Thus the clusterings may arise from recombination of Au interstitials with solute Au (defects other than free vacancy): The recombination of Au interstitials with free vacancies leads to a kinetic law of pseudo-first order rather than

that of second-order experimentally observed, owing to the possibility that the concentration is much larger for Au solute than for vacancy. These results suggest that all the vacancies are trapped by interstitials Au atoms before the clustering begins to start at low T_a below $T_c(1)$ and the binding energy between vacancy and interstitial is probably large. That is, the free vacancy plays no important role in determining the rate of clustering.

2. Precipitation

As the temperature T_a rises, the vacancy trapped by Au interstitial at low temperatures may begin to dissociate into a vacancy and an interstitial which are in single states. Moreover, even the associated Au atoms (complexes, presumably doublets or triplets), less mobile defects, can diffuse to produce the more stable precipitates, causing the resistivity decrease for instance in ranges C and D. It is difficult to understand the growth mechanism of precipitates from the value of exponent m in the Johnson-Mehl-Avrami type of equation, $f = 1 - \exp(-bt^m)$ ⁽¹⁹⁾. We use therefore the kinetic laws—i.e. zero-order and first-order—observed for the temperature ranges C and D (Table 1), to discuss the precipitation mechanism. If the effective valency (Z_{eff}) of vacancy is -4 , then the vacancy may be more attractive to interstitial Au ($Z_{eff} = +1$) than to substitutional Au ($Z_{eff} = -3$) or solvent atom ($Z_{eff} = 0$). We propose a model, eq. (1), to account for the kinetics in the ranges C and D, assuming that although the vacancies are attractive to the interstitials the interaction energy between the vacancies and precipitate nuclei is very small:

where i , v and i^* are respectively the concentrations of unassociated Au interstitials, the vacancies, and the interstitials trapped by vacancies (interstitial-vacancy pairs); P is the precipitate nuclei whose number is fixed immediately after quenching; and k 's are the corresponding rate constants. Reaction (a) represents the equilibrium between association of interstitial (i) with vacancy (v) due to correlated motion of freely migrating i -atoms to v and dissociation of the resulting i^* -complexes. Reaction (b) shows a precipitation of Au by migration of i^* to P of fixed number, and a return of v to the matrix solid solution (vacancy-turnover model). These vacancies are soon trapped by interstitial Au atoms (forward reaction in the (a)), owing to the large interaction between i and v . The fact that at low T_a below $T_c(1)$ we cannot observe experimentally first-order kinetics with activation energy comparable to that (Q_d) for diffusion, indicates that no simple migration of the free interstitials to clusters occurs in the pre-precipitation stage. Similarly, we ignore a simple reaction, $i \rightarrow P$, for the precipitation at T_a above $T_c(1)$ (in ranges C and D). The other reaction, $v \rightarrow \text{sinks}$, was also neglected, based on the proposal that the efficiency of vacancy sinks (dislocations) was low

in lead⁽²⁰⁾. Thus, the vacancies can possess long life-time enough for the precipitates to grow appreciably before the process ends. The simple model alone that the i^* migrates to the P is insufficient to describe the zero-order reaction. Equation (1) is formally identical with enzyme-catalyzed reaction⁽²¹⁾. This model is also same as that used previously for interpreting the clustering in a Pb–Mg alloy⁽¹⁵⁾, except that the role of vacancy differs in the two alloys: The vacancy is an inhibitor (negative catalyst) in the Pb–Au alloys, while it is an accelerator (catalyst) in the Pb–Mg alloy.

The kinetic equations for the reactions (a) and (b) are written by

$$di/dt = k_2 i^* - k_1 i v \quad (2)$$

$$di^*/dt = k_1 i v - k_2 i^* - k_3 i^*. \quad (3)$$

The total Au concentration, $N = i + i^*$, is described by

$$dN/dt = (di/dt) + (di^*/dt) = -k_3 i^*. \quad (4)$$

The various rate constants may be written by

$$k_1 = 48\nu \exp(-E_m^i/kT), \quad (5)$$

$$k_2 = 8\nu \exp[-(E_m^i + B^i)/kT], \quad (6)$$

$$k_3 = \alpha\nu\lambda^2 \exp[-(E_m^i + B^i)/kT], \quad (7)$$

where 48 and 8 are the combinatory numbers for association and dissociation of interstitial-vacancy pair in *fcc* lattice in which the interstitial is assumed to occupy the octahedral site, ν the vibrational frequency, λ the jump distance, α the density of precipitate nuclei, the values assigned to these constants are $\nu = 10^{13}$, $\lambda^2 = 10^{-15}$ cm² and $\alpha = 10^{10}$ cm⁻²; E_m^i is the migration energy of interstitial, and B^i the binding energy between interstitial and vacancy. Equilibrium constant of the reaction (a) is

$$K \equiv i^*/iv \equiv k_1/k_2 = 6 \exp(B^i/kT). \quad (8)$$

From an assumption that the concentrations are much smaller for the vacancy than for the solute Au atom, a steady-state approximation can be set up for interstitial-vacancy complex: $di^*/dt = 0$. This approximation lets us obtain the i^* -value as

$$i^* = k_1 i v_0 / (k_1 i + k_2 + k_3), \quad (9)$$

with another assumption that the law of conservation holds for the total concentration of vacancy: $v = v_0 - i^*$, where v_0 is the concentration of quenched-in vacancy. Moreover, we assume that the rate-determining step of the precipitation is the reaction (b), since the k_3 is much smaller than k_1 and k_2 ; and k_3 is ignored as compared with k_1 and k_2 in eq. (9). Substitution of eq. (9) into eq. (4) gives

$$dN/dt = -k_3 K i v_0 / (K i + 1). \quad (10)$$

Experimentally we measure the resistivity of Pb containing defects i , i^* and v :

$$\Delta\rho(t) = i\Delta\rho_i + i^*\Delta\rho_{i^*} + v\Delta\rho_v, \quad (11)$$

where $\Delta\rho$'s are the residual resistivity due to the defects of unit concentration. A considerable simplification is in-

troduced if we assume

$$\Delta\rho_i \equiv \Delta\rho_{i^*}. \quad (12)$$

This assumption is similar to that used by Corbett *et al.*⁽²²⁾ to interpret the resistivity recovery in electron-irradiated Cu. Furthermore, since the initial Au-concentration (N_0) in the solid solution is 4.20×10^{-4} , we assume

$$i\Delta\rho_i + i^*\Delta\rho_{i^*} \gg v\Delta\rho_v, \quad (13)$$

using the experimental results obtained by the previous workers, $v_0 = 1.35 \times 10^{-5}$ and $\Delta\rho_v = 25$ nΩm/at%⁽²³⁾; and $\Delta\rho_{Au} = 45$ nΩm/at%⁽²⁴⁾. Equation (11) therefore reduces to

$$\Delta\rho(t) = \Delta\rho_i (i + i^*). \quad (14)$$

Actually we measured the $(\Delta\rho(t)/\Delta\rho_i)$ -versus- t relations. Since $\Delta\rho_i = \Delta\rho_i(i_0 + i_0^*)$,

$$\Delta\rho(t)/\Delta\rho_i = N/N_0, \quad (15)$$

where i_0 and i_0^* are the initial values of i and i^* , and $N_0 = i_0 + i_0^*$. Equation (10) then is applicable to explain the experimental results.

The K in eq. (8) decreases sharply with increasing temperature, giving different relative values of rate constants (k 's), for large B^i . Thus, eq. (10) leads to two kinds of rate equations arising from the k 's in different temperature regions.

Case 1: For $Ki \gg 1$, eq. (10) reduces to

$$dN/dt = -k_3 v_0, \quad (16)$$

which represents a zero-order reaction, and shows that all the vacancies are in the form of interstitial-vacancy complex.

Case 2: For $Ki \ll 1$, eq. (10) reduces to

$$dN/dt = -k_3 K v_0 i, \quad (17)$$

which represents a first-order reaction. Case 2 occurs in a temperature region higher than that for Case 1, since the K decreases with increasing temperature. Even in the low- T_a region where Case 1 is occurring, Case 2 will take place in the later stage of the process, since the value i decreases as the precipitation proceeds. Thus, the eq. (1) can illustrate the precipitation kinetics in the T_a -ranges C and D (above $T_c(1)$). That is, the vacancies play an important role as a negative catalyst in determining the kinetics of Pb₃Au precipitation. This model assigns the Q_p (84.1 kJ/mol) for the range C to $(E_m^i + B^i)$ and the Q_p (42.7 kJ/mol) for the range D to E_m^i , giving $B^i = 41.4$ kJ/mol.

It is concluded that the precipitation kinetics is more complicated in Pb–Au alloys than in Pb–Ag alloys or in Pb–Ni alloys. This situation in Pb–Au alloys is possibly due to the large value of B^i , which leads to sharp temperature-dependence of equilibrium between association of interstitial with vacancy and dissociation of the interstitial-vacancy pair, and allows long-life of the vacancy. A simple consideration taking account of only effective valency of the various defects, however, cannot explain the difference between Pb–Au alloy and Pb–Ag alloy in the role of vacancy playing for the precipitations.

V. Summary

The kinetics of precipitation in Pb–Au alloys as quenched from 488 K was monitored by observing the resistivity of alloys containing 0.042–0.075 at% Au, aged over the temperature range 195 to 488 K.

(1) The Au interstitials, present in solid solutions at high temperatures above Pb_3Au solvus, can be frozen-in by quenching the alloys from 448 K into iced water.

(2) For both isochronal- and isothermal-aging, the decomposition of the super-saturated solid solutions occurs firstly with anomalous increases in resistivity in low- T_a range below 335 K (0.042 at% Au alloy) or 380 K (0.075 at% Au alloy).

(3) This increase of resistivity in the early stage of aging is indicative of clustering of Au atoms at these low temperatures. Two types of clusters possessing different thermal stability form during aging at T_a below 280 K (0.042 at% Au alloy). The metastable solid-solubility curves were determined for these clusters. The nature of the clusters, however, is not clear at present. The free vacancies play no important role in determining the clustering kinetics, since all the vacancies are possibly trapped by highly-mobile Au-interstitials immediately after quenching.

(4) The Pb_3Au precipitation occurs with usual resistivity decrease during isothermal aging at high T_a above 335 K (0.042 at% Au alloy), but its kinetic law and activation energy vary according to whether the T_a is below or above 390 K. The vacancies play an important role in determining the precipitation kinetics in this T_a range, since the vacancies trapped by Au interstitials immediately after quenching become capable of dissociating to isolated vacancies with rising T_a . A model based on vacancy-catalyzed reaction, allowing turnover and long-life of vacancy, can demonstrate two varieties of Pb_3Au precipitation kinetics. This model yields a value of 41.4 kJ/mol for the binding energy between Au interstitial and vacancy.

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