Kinetics of Precipitation of Nickel from Lead-Nickel Solid Solution

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Kinetics of Ni precipitation in Pb-alloys containing 0.013–0.213 at%Ni was studied by measuring the resistivity of the alloys aged after quenching from 558 K. During an isochronal aging (45 s), the resistivity decreases roughly in a single stage and then increases with rising temperature. The resistivity decreases in two distinct stages during isothermal aging of Pb–0.070 at%Ni alloy below 303 K. The precipitation in the initial stage (I_A) is a first-order reaction with an activation energy of 49.9 ± 3.0 kJ/mol. The second stage (II_A) is also a first-order reaction, but has a different value of activation energy, 100.3 ± 4.0 kJ/mol. At 303 K or above, the resistivity decreases in a single stage (I_B) during isothermal aging. The kinetics of stage I_B is described by Johnson-Mehl's equation with a value of $2/3$ as the constant n . The activation energy for this stage is found to be 80.9 ± 3.0 kJ/mol.

It is supposed that the precipitations in three stages I_A , II_A and I_B are controlled by diffusion of nickel interstitials, substitutionals and interstitial-vacancy pairs, respectively.

The solubility of nickel in solid lead determined in the present work was much lower than a previously accepted value.

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I. Introduction

A transition metal Ni is one of "fast diffusers" in solid lead⁽¹⁾⁽²⁾. It seems to be well established that the rate of precipitation of the fast diffusers from lead containing these impurities is connected with their volume diffusion^{(3)–(5)}. Nickel diffuses in lead by a pure interstitial mechanism⁽²⁾ at temperatures from 481 to 600 K: Interstitial Ni atoms are not trapped by vacancies at temperatures of diffusion⁽²⁾ or electromigration⁽⁶⁾ experiments. However, there is the possibility that the motion of nickel is suppressed by trapping of the interstitial Ni atoms at vacancies below solvus temperatures for Ni. Thus the kinetics of Ni precipitation may be affected by the behavior of this trapping, and hence by the aging temperature.

The present paper describes a resistometric

study on kinetics of precipitation of nickel from lead-nickel solid solution below solvus temperatures for nickel. During the present study, it was required to re-examine the solubility of nickel in solid lead. The Ni solvus obtained is also reported here.

II. Experimental Procedure

Techniques for preparation of alloys and measurements of resistivity were mainly similar to those described previously⁽⁵⁾. Lead-nickel alloys containing 0.013 to 0.213 at%Ni were prepared in evacuated silica capsules (2.7×10^{-3} Pa) at 973 K from 99.999% lead and 99.99% nickel. The alloy ingots were annealed at 558 K for 360 ks (100 h) in the capsules for homogeneization. The results of determination of Ni concentration in the alloy give the following values; 0.013, 0.045, 0.056, 0.070, 0.098 and 0.213 at%Ni. Wire specimens, 1.7 mm in diameter and 75 mm in length, were prepared by cold rolling and drawing the alloy ingots. Before aging, the specimens were quenched into iced water after solution-annealing at 558 K for 3.6 ks (1 h). Two methods of aging treatment were employed; (a) isochronal aging at tem-

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peratures $T_a = 195\text{--}563\text{ K}$ and (b) isothermal aging at $T_a = 195\text{--}338\text{ K}$. The specimens were immersed in liquid nitrogen during the resistivity measurements. The resistivity of specimens was expressed as ρ/ρ_0 where ρ_0 is the resistivity in the as-quenched condition, and ρ is that at the state aged for a time t .

III. Experimental Results

1. Isochronal aging

Figure 1(a) shows the result of isochronal aging (40 s) of a Pb-0.070 at%Ni alloy with increasing temperature with an interval of 10 K from 195 K to 563 K. Figure 1(b) gives a nu-

Fig. 1 Isochronal aging (40 s) curve for resistivity of Pb-0.070 at%Ni alloy quenched from 558 K: Curve (a). Curve (b) is numerical derivative of curve (a).

Fig. 2 Isochronal aging (40 s) curves for resistivity of Pb alloys containing 0.013, 0.045 and 0.070 at%Ni. All of the alloys were aged for 10.8 ks at 328 K after quenching from 558 K.

Fig. 3 Solubility of nickel in solid lead.

merical derivative of curve (a). With increasing temperature, the resistivity decreases first at 230–375 K roughly in a single stage, and then increases at 375–553 K. The as-quenched resistivity ρ_0 is restored at 553 K, which is regarded as the solvus temperature for Ni in this alloy. Figure 2 shows parts of resistivity-increase in an isochronal aging curve similar to Fig. 1(a), for several alloys of various concentrations of Ni. These restoring temperatures obtained here were plotted against the Ni concentration of the alloys in Fig. 3. The resulting Ni solvus is shown by a curve accompanying open circles. The temperature dependence of the present solubility of Ni in solid lead was found to be expressed at temperatures below 570 K by

$$c_e = (770 \pm 200) \exp [-(41900 \pm 1000)/RT], \quad (1)$$

where c_e is in at%Ni, and R the gas constant in J/(mol·K).

2. Isothermal aging

In Fig. 4, typical aging-curves at various temperatures T_a are shown for Pb-0.070 at%Ni alloy. The resistivity decays in two distinct stages (I_A and II_A) below 303 K (in range A). At 303 K or above (in range B), the resistivity decreases in a single stage I_B . In this figure, t_f^I is the time to finish the first stage I_A or I_B , and t_s^{II} and t_f^{II} are respectively times for initiation and termination of the second stage II_A .

Fig. 4 Isothermal aging curves at various temperatures (T_a) for resistivity of Pb-0.070 at %Ni alloy quenched from 558 K. Arrow ↓ shows example of time t_f^I to finish first stage I_A or I_B; †, time t_s^{II} to initiate second stage II_A; and ‡, time t_f^{II} to finish stage II_A.

3. Kinetic law

The fractional resistivity change after time t , f^I , was determined from Fig. 4 for stage I_A or I_B: $f^I = (\rho_0 - \rho) / (\rho_0 - \rho_f^I)$, where ρ_f^I is the resistivity to finish stage I_A or I_B, that is, the resistivity at t_f^I . In Fig. 5, the logarithm of $(1 - f^I)$ was plotted against t for stage I_A. This figure exhibits that a simple exponential-decay occurs in stage I_A. For stage I_B, however, the logarithm of $(1 - f^I)$ vs t relation is not linear: No simple exponential-decay occurs in stage I_B (the figure is not shown in this paper). Thus, $\log \log [1 / (1 - f^I)]$ was plotted against the logarithm of t for stage I_B in Fig. 6. This plot indicates that the I_B-decay can be expressed by Johnson-Mehl's equation,

$$f^I = 1 - \exp(-bt^n), \quad (2)$$

with a n -value of 2/3 on the average. This value of n suggests that the Ni atoms in Pb are attracted to dislocations in a manner similar to

Fig. 5 Logarithms of remaining fractional decay $[1 - f^I = (\rho - \rho_f^I) / (\rho_0 - \rho_f^I)]$ as a function of aging time (t) in stage I_A, for Pb-0.070 at %Ni alloy.

Fig. 6 Plots of $\log \log [1 / (1 - f^I)]$ against $\log t$ for stage I_B of Pb-0.070 at %Ni alloy.

the case of interstitial carbon atoms in Fe⁽⁷⁾. The fractional resistivity change after t , f^{II} , was determined for stage II_A from Fig. 4: $f^{II} = (\rho_f^I - \rho) / (\rho_f^I - \rho_f^{II})$, where ρ_f^{II} is the resistivity to finish stage II_A, that is, the resistivity at t_f^{II} . Figure 7 shows the logarithm of $(1 - f^{II})$ plotted against $(t - t_s^{II})$. This figure indicates that the II_A-decay obeys a simple exponential kinetics.

Fig. 7 Logarithms of remaining fractional decay $[1 - f^{II} = (\rho - \rho_f^{II}) / (\rho_f^I - \rho_f^{II})]$ as a function of aging time $(t - t_s^{II})$ in stage II_A, for Pb-0.070 at %Ni alloy.

4. Activation energy

Figure 8 shows Arrhenius plots of $t_{0.5}^I$ and t_f^I at T_a not higher than 273 K, where $t_{0.5}^I$ is the time to complete one-half of stage I_A and can be determined from Fig. 4. The $t_{0.5}^I$ and t_f^I reflect the rate constants in the central and later parts of the first-order reaction occurring in stage I_A. These two plots yield almost identical values (50.2 and 48.5 kJ/mol) of activation energy (Q), and the average value 49.4 ± 3.0 kJ/mol is taken as Q for the stage I_A. Figure 8 shows also the Arrhenius plots of t_s^{II} and t_f^{II} which reflect the

Fig. 8 Arrhenius plots of $t_{0.5}^I$, t_f^I , t_s^{II} and t_f^{II} in stages I_A and II_A, for Pb-0.070 at%Ni alloy.

Fig. 9 Arrhenius plots of $t_{0.5}^I$ and t_f^I in stage I_B, for Pb-0.070 at%Ni alloy.

rate constants in the initial and later parts of the first-order reaction occurring in stage II_A. These two plots yield almost identical values (99.6 and 101 kJ/mol) of Q , and the average value 100.3 ± 4.0 kJ/mol is taken as Q for the stage II_A. Arrhenius plots of $t_{0.5}^I$ and t_f^I at $T_a = 303$ –338 K are shown in Fig. 9, where $t_{0.5}^I$ is the time to complete one-half of stage I_B. The value of $t_{0.5}^I$ cannot be determined at T_a above 323 K, because of a rapid progress of this stage. The plots give an average value of Q , 80.9 ± 3.0 kJ/mol, for the first-order reaction in stage I_B.

IV. Discussion

1. Solubility of nickel in solid lead

It has been repeatedly proposed that the solubility of nickel in solid lead should be reinvestigated⁽⁸⁾⁽⁹⁾, although the Ni solvus was determined by the magnetic method and 0.68 at% (0.195 mass %) Ni was accepted as the maximum solubility of nickel in solid lead at 600 K⁽¹⁰⁾. These proposals are based on the facts that 0.38 at% Ni is found as a eutectic composition at 597 K near Pb in the Pb–Ni system⁽¹¹⁾, and that a considerable grain refinement occurs in Pb–Ni alloys containing about 0.1 at% Ni⁽⁹⁾. A value of the eutectic composition, 0.46 at% Ni, reported more recently⁽¹²⁾ is also lower than the maximum solubility accepted previously. The present values

Fig. 10 Decrement of ρ/ρ_0 due to completion of precipitation at 293 K after quenching from 558 K, $1 - (\rho^I/\rho_0)$, as a function of Ni concentration of alloys.

for the solubility shown in Fig. 3 are an order of magnitude lower than the previously accepted value, but is not inconsistent with both the eutectic compositions described above and with a maximum solubility of Ni in solid lead, 0.21 at %Ni, reported by Ono⁽¹³⁾. In Fig. 10 the decrement of ρ/ρ_0 due to the completion of precipitation of Ni at 293 K after quenching from 558 K, $1 - (\rho_f^{\text{II}}/\rho_0)$, was plotted against the Ni concentration of the alloys. The resulting curve prefers a value of 0.087 at %Ni given from eq. (1) rather than 0.317 at %Ni reported previously⁽¹⁰⁾ as the solubility of nickel in solid lead at 558 K.

2. Precipitation kinetics

Three different values were observed for the activation energy in different stages of precipitation of nickel from the Pb–Ni solid solution. The value 49.4 kJ/mol for stage I_A is fairly in agreement with that 44.4 kJ/mol⁽²⁾ for diffusion of interstitial Ni atom, and the value 100.3 kJ/mol for stage II_A agrees well with 101.3 kJ/mol⁽¹⁴⁾ for self-diffusion of lead. Since both stages I_A and II_A are of simple first-order reaction, it is supposed that the Ni transport during precipitation in these stages is controlled by the migration of interstitials and substitutionals, respectively, to a fixed number of precipitate nuclei. The value of activation-energy, 80.9 kJ/mol, for stage I_B is in fair agreement with that 87.0 kJ/mol found by Rossolimo *et al.*⁽³⁾ for precipitation of AuPb₃ from Pb–Au solid solution. These authors considered from this activation energy that the precipitation of AuPb₃ is controlled by diffusion of interstitial-vacancy(*iv*) pairs or diinterstitial-vacancy(*i₂v*) clusters (split interstitials), where *i* is the interstitial Au atom and *v* the vacancy. Thus the present value of activation energy is also attributed to activation energy for diffusion of interstitial Ni atom-vacancy(*iv*) pairs or *i₂v* cluster. Since the kinetic law for this stage can be described by Johnson-Mehl's equation with $n=2/3$, the *iv* pairs or *i₂v* clusters are considered to be attracted to dislocations during the precipitation.

Diffusivity⁽²⁾ and electromigration⁽⁶⁾ data suggest that most of the dissolved Ni is in an interstitial state and moves in a simple inter-

stitial mechanism above solvus temperatures for Ni. The present precipitation data, however, reveal that attractive interactions are present between interstitial Ni atoms and vacancies: Interstitials may be trapped by vacancies with a reaction, (a) $i + v \rightarrow s$, or (b) $i + v \rightarrow iv$, depending upon the aging temperature below the solvus temperatures for Ni, where *s* is a substitutional Ni atom. For simplicity we ignore the formation of higher order defects or clusters (e.g., *i₂v* cluster) in the present discussion. We suppose that in the condition as-quenched from 558 K the nickel atoms are primarily in the interstitial state. The concentration of the interstitial atom may be much higher than that of vacancy at the beginning of aging below 303 K. Then the first stage of the precipitation would occur with transport of the excess free interstitials to the precipitate nuclei (stage I_A). At the end of stage I_A, only the interstitials trapped by vacancies remain untransported to the nuclei. These interstitials may become substitutionals due to reaction (a). The substitutional atoms may precipitate in II_A, the later stage of aging. Assuming that formation entropy is larger for *iv* pair than for *s*, we suppose that the interstitials are trapped by vacancies to produce *iv* pairs with reaction (b) rather than with (a), at a temperature of 303 K or above (in range B). These *iv* pairs may precipitate in stage I_B. Since only single stage I_B occurs in range B, most of the interstitials must be trapped by vacancies at the beginning of the aging. The equilibrium concentration of vacancy in pure lead⁽¹⁵⁾ at 333 K—namely, a temperature above 303 K—is about 10^{-7} , which is too low in concentration to trap most of the interstitials quenched-in from 558 K when the vacancy can trap only one interstitial Ni atom to produce *iv* pair. Thus it is again supposed that an attractive interaction is present between the interstitials and the vacancies, and the vacancy concentration may be higher in the Pb–Ni alloys than in the pure lead.

On the basis of this model for precipitation, the rate constants (k_{IA} , k_{IIA} and k_{IB}) for the precipitations in stages I_A, II_A and I_B may be given by the expressions

$$k_{\text{IA}} = A_1 \exp(-E_i/kT), \quad (3)$$

$$k_{\text{IIA}} = A_2 \exp [-(E_i + B_s)/kT] \quad (4)$$

and

$$k_{\text{IB}} = A_3 \exp [-(E_i + B_{iv})/kT], \quad (5)$$

where A_1 , A_2 and A_3 are the frequency factors, E_i the migration energy of the free interstitial nickel atom, and B_s and B_{iv} the binding energies between interstitial nickel atom and vacancy participating in the formation of substitutional nickel atom and interstitial-vacancy pair, respectively. Thus, three experimental values of activation energy for each stage are assigned as follows: $E_i = 49.4$ kJ/mol, $E_i + B_s = 100.3$ kJ/mol, and $E_i + B_{iv} = 80.9$ kJ/mol. Therefore, we have $B_s = 50.9$ kJ/mol and $B_{iv} = 31.5$ kJ/mol.

V. Conclusion

(1) During an isochronal aging (40 s), the resistivity decreases first roughly in a single stage and then increases with rising temperature up to a restoring temperature, at which the as-quenched resistivity is recovered. The restoring temperature, which is regarded as the solvus temperature for nickel, is not in agreement with that accepted previously.

(2) The resistivity decreases in two distinct stages during isothermal aging of Pb-0.070 at% Ni alloy below 303 K (in range A). The precipitation in the initial stage (I_A) is a first-order reaction with an activation energy of 49.4 ± 3.0 kJ/mol. The second stage (II_A) is also a first-order reaction, but has a different value of activation energy, 100.3 ± 4.0 kJ/mol.

(3) At 303 K or above (in range B), the resistivity decreases in a single stage (I_B) during isothermal aging of the alloy. The precipitation kinetics of this stage is described by Johnson-Mehl's equation with a value of $2/3$ as the constant n . The activation energy is found to be 80.9 ± 3.0 kJ/mol for this stage.

(4) It is supposed that the precipitations in stages I_A and II_A are controlled by diffusion of free interstitial and substitutional Ni atoms, respectively, to precipitate nuclei, while that in stage I_B is due to migration of interstitial Ni atom-vacancy pairs to dislocations.

(5) From the present model for precipitation, the binding energy between interstitial nickel atom and vacancy was estimated to be 31.5 kJ/mol with production of interstitial-vacancy pair and 50.9 kJ/mol with that of substitutional nickel atom.

(6) The solubility of nickel in solid lead was redetermined in the present work. The resulting values were an order of magnitude lower than the previously accepted values.

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