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Kinetics of short-range order formation in the ternary Au–Ag–Pd alloys

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Abstract

The kinetics of formation and destruction of short-range order (SRO) were investigated in the ternary $Au_{40}Ag_{40}Pd_{20}$ alloy using the residual resistometry. The changes in residual electrical resistivity were measured during down-quenching (DQ) and up-quenching (UQ)[1] cross-over annealing experiments. The quantitative analysis of the resistivity data showed that three kinetic processes are involved in the short-range ordering and disordering process. The results agree qualitatively with the Yu–Lucke model for the kinetics of SRO in the fcc ternary alloys. However, the kinetic parameters derived from the cross-over experiments during ordering and disordering was found to be complicated and different from the unidirectional isothermal kinetics. These differences suggest that the reaction paths during ordering and disordering are different.

Keywords: Au–Ag–Pd alloys; Short-range order; Quenching

1. Introduction

The Au–Ag–Pd alloys have been investigated for various technological applications, e.g. biomedical applications, electrical contacts, jewellery, etc. Many properties of these alloys are dependent on the short-range order (SRO), e.g. Naidu and Houska considered SRO to be a possible mechanism in the unusually large degree of solid solution strengthening of these alloys [1]. This paper deals with the ternary alloys obtained by a partial substitution of Au and Ag with Pd, keeping their concentration equal. Pd is a significant constituent of many commercial alloys based on Au and Ag. It forms a series of continuous solid solutions with Au and Ag over a wide range of compositions and temperatures [2].

The interest in the study of SRO in the ternary Au–Ag–Pd alloys stems from the fact that it is free from intermediate phases or other complications at low temperatures, has close obedience to the Vegard's rule and Au, Ag, and Pd have almost similar atomic sizes, which indicates a close approach to ideality [2]. The kinetics of SRO have been investigated in many binary alloys using the residual resistometry whereas, the ternary alloys have been rarely studied [3–8]. It has been found that the SRO kinetics in $Au_{40}Ag_{40}Pd_{20}$ follow the three-exponential law whereas, the two-exponential kinetics were found in the case of $Au_{25}Ag_{25}Pd_{50}$ [4,5]. It has also been seen that the results of isothermal experiments in these alloys can be explained by the application of different kinetic laws [6–8], leaving the actual question about the nature of kinetics unresolved. Deviations from the theory have also been observed in some cases [5,6,8,9].

The cross-over effect has often been used to study the nature of the kinetics in binary alloys but rarely for ternary alloys [10–12]. It occurs only when the SRO evolution involves two or more simultaneous processes with different time constants and yields important information about the intermediate states through which an alloy undergoes during the isothermal annealing.

We report here the results of the cross-over experiments performed on the ternary $Au_{40}Ag_{40}Pd_{20}$ alloy under equilibrium conditions. A theoretical formulation of the cross-over kinetics is given. Finally, the results have been interpreted in terms of the theoretical framework and discussed from the point of view of the kinetics of SRO in fcc ternary alloys.

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[1] In up-quenching (UQ) experiments $T_q < T_a$ and in down-quenching (DQ) experiments $T_q > T_a$. T_q and T_a are the quenching and annealing temperatures.

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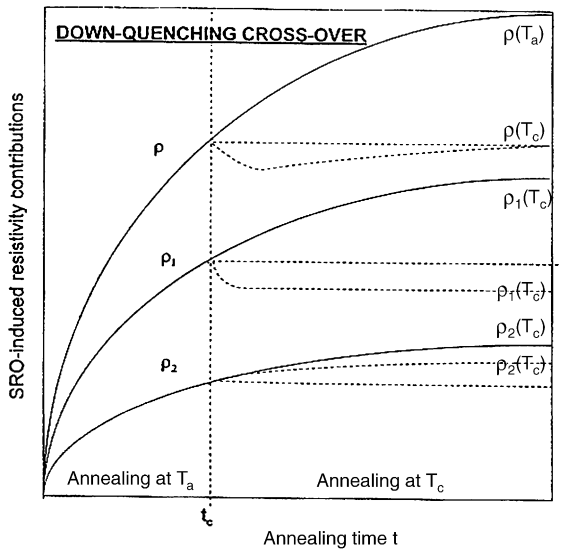

Fig. 1. The schematic diagram of the DQ-cross-over annealing experiment.

2. Theory

The schematic diagram of a DQ-cross-over annealing experiment is shown in Fig. 1. For simplicity, the total resistivity ρ is here assumed to comprise of two contributions ρ_1 and ρ_2.[2] In this experiment, first a DQ-isothermal annealing experiment is carried out after quenching from temperature T_q. The isothermal annealing at temperature T_a is interrupted after time t_c at which the instantaneous value of resistivity becomes equal to the equilibrium value of the resistivity ρ^c at temperature T_c. It is followed by an UQ-isothermal annealing at temperature T_c and the sample is annealed till a constant resistivity value ρ^c is reached. In the UQ-cross-over experiment, first an UQ-isothermal experiment is performed. The annealing at temperature T_a is interrupted after time t_c, at which the instantaneous value of the resistivity becomes equal to the equilibrium resistivity corresponding to temperature T_c. The schematic diagram of an UQ-cross-over experiment can be drawn similarly and will lead to a resistivity maximum. The schematic diagrams can be easily extended for the case of three or more simultaneous processes. The resistivity change during a cross-over experiment can be explained as follows.

Consider the resistivity change $\Delta\rho$ at time $t = 0$ during the DQ-isothermal annealing at $T = T_a$, given by

$$\Delta\rho = \rho(t) - \rho_0 = \sum\nolimits_i \Delta\rho_i = \sum\nolimits_i A_i \left(1 - \exp\left(-\frac{t}{\tau_i(T_a)}\right)\right) \quad (1)$$

The resistivity after time t_c becomes equal to the resistivity corresponding to the temperature $T = T_c$. Therefore, the resistivity change $\Delta\rho^c$ corresponding to the time t_c is

$$\Delta\rho^c = \sum\nolimits_i \Delta\rho_i^c = \sum_i A_i \left(1 - \exp\left(-\frac{t_c}{\tau_i(T_a)}\right)\right) \quad (2)$$

This is followed by an UQ-isothermal annealing at the temperature $T = T_c$. The resistivity change $\Delta\rho'$ is given by

$$\Delta\rho' = \sum\nolimits_i \left[\Delta\rho_i^c + A_i' \left(1 - \exp\left(-\frac{t'}{\tau_i'(T_c)}\right)\right)\right] \quad (3)$$

where $t' = t - t_c$ and the new amplitudes A_i' and the relaxation times $\tau_i'(T_c)$ are given by

$$A_i' = A_i \exp\left(-\frac{t_c}{\tau_i(T_a)}\right),$$

$$\tau_i'(T_c) = \tau_i(T_a) \exp\left(-\frac{H_{SRO}^i}{k_B(T_c - T_a)}\right) \quad (4)$$

At time $t = \infty$, it follows from Eq. (3) that:

$$\Delta\rho'(t = \infty) = \sum\nolimits_i (\Delta\rho_i^c + A_i') = \sum\nolimits_i \Delta\rho_i^c,$$

$$\text{i.e.} \sum_i A_i' = 0 \quad (5)$$

The application of this equation shall lead to the interpretation of the results (as demonstrated in Section 4).

3. Experimental

The details of the sample preparation, annealing and quenching apparatus used in this study have been described in [3]. The alloy was kindly supplied by Degussa(Hanau). The given purity of the alloy materials was 99.999%. The chemical composition of the alloy determined by electron probe microanalysis (EPMA) was nearly $Au_{40}Ag_{40}Pd_{20}$. The microanalysis revealed that the homogeneity variation of the alloy was <1 at.%. The resistivity of the alloy samples was measured after each annealing or quenching step. The samples were transferred to a cryostate at a constant liquid nitrogen temperature. This enabled to keep the contribution of phonons to the resistivity constant. The measurements were performed relative to a reference sample of the same material as the actual sample. The reference sample was placed besides the actual sample in the cryostate. The resistivity of the sample was measured with the help of a Thompson bridge to eliminate the effect of contact voltages. The accuracy of the measurements was ±5%.

4. Results

Fig. 2 shows the normalized resistivity change as a function of the annealing time for two different DQ-cross-over experiments. A minimum is observed in both figures. A comparison of the two figures shows the following features:

[2] ρ_1 and ρ_2 are the resistivity contributions due to the two kinetic processes occurring during SRO formation.