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Detection of short- and long-range order in Cu-Pt alloys

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Both short-range order (SRO) and long-range order (LRO) have been investigated in Cu-Pt alloys at various temperatures and compositions by means of the electrical resistivity measurement technique. It can be shown that stable long-range-ordered equilibrium states can be achieved by thermal treatment. The effects of SRO and LRO can be separated for the nonequiatomic compositions by taking advantage of the different characteristics of the resistivity change on short-range and long-range ordering.

I. INTRODUCTION

Effects of order in alloys generally depend strongly on temperature. The formation of long-range order (LRO) is a question of low enough temperature with respect to the critical temperature because of an increasing driving force towards ordering with increasing distance from the phase boundary. On the other hand, the experimental observation of LRO effects is linked to a high enough temperature to guarantee the atomic mobility for the rearrangement of the alloy atoms.

The formation of short-range order (SRO) frequently has been investigated for temperatures above the phase boundary or in systems without any long-range-ordered phase. Because of the rather small atomic rearrangements needed for the formation of SRO compared to LRO, SRO relaxation in general is much faster than LRO relaxation.

Three questions which are most important for any systematic investigation of ordering effects arise from these facts.

1. Can definite equilibrium LRO states be established by thermal treatment in considerable annealing times?
2. Can states of pure SRO be prepared even in the regime of LRO utilizing the different relaxation behavior of LRO and SRO?
3. How does the occurrence of SRO and LRO depend on the pretreatment (mechanical and/or thermal) of the alloy?

The Cu-Pt system turned out to be well suited for this investigation because for the Cu-rich composition (35 at. % Pt) SRO and LRO lead to resistivity changes of different signs so that they can be distinguished. Furthermore, for these compositions the formation of LRO is rather weak so that the SRO effects are not obscured by a strong LRO. On the other hand, the Pt-rich alloy (70 at. % Pt) and even more the equiatomic alloy show a strong resistivity change obviously due to LRO, so that the question concerning the LRO equilibrium states can be answered. In addition an interesting inversion of the sign of the resistivity change on SRO can be observed when going from Cu-rich to Pt-rich alloys.

II. EXPERIMENTAL

The samples, foils of 0.2 mm thickness, were prepared by cold rolling with intermediate anneals in a purified argon atmosphere. After annealing the foils were quenched in cold water. The quench could be done very quickly so that the cooling rate was more than 1000 K/s.

The resistivity measurements were performed at liquid-nitrogen temperature under exactly constant conditions so that the relative change of resistivity could be determined with a very high accuracy. All systems were first preannealed after the cold rolling at a temperature just above the phase boundary for one hour. The first experiments were a series of isochronal anneals starting at 200 °C up to 800 °C in steps of 50 °C and back to 300 °C with annealing times of 20 min for each temperature. To check the equilibrium, for certain temperatures isothermal anneals were performed in addition. The experimental techniques are discussed in detail in Ref. 1.

III. RESULTS AND DISCUSSION

The results for the two compositions where strong LRO occurs are shown in Figs. 1 and 2. In the equiatomic alloy at about 300 °C a drastic decrease of resistivity by 80% obviously indicates the formation of LRO. After a minimum at 540 °C the resistivity increases again, which must be connected with the destruction of LRO. Above the critical temperature which is at about 820 °C (Refs. 2 and 3) the resistivity maintains a constant value which is exactly the same as before the anneals. This demonstrates the good quality of the quenching procedure used. SRO effects obviously are too small for observation or nonexistent above T_c.

The triangles in Fig. 1 show the effect of isochronal annealing at falling temperatures (reversed isochrone): below 650 °C the decreasing concentration of thermal vacancies prevents the ordering process to be completed. The question is now whether the increasing value of resistivity between 540 °C and T_c are equilibrium values reflecting the temperature dependence of the LRO parameter. This has been checked by an isothermal annealing experiment at 650 °C: The change of resistivity with time (see inset of Fig. 1) clearly shows that an equilibrium state is established although the results of Irani and Cahn[4] suggest a nucleation and growth reaction (type I) for the ordering reaction in equiatomic and Pt-rich Cu-Pt alloys. The results on isochronal annealing are in good agreement with an investigation by Torfs *et al.*[5]

Figure 2 shows the change in resistivity for Cu–70 at. % Pt. A slight decrease can be seen already at 200 °C, but the drastic drop which indicates formation of LRO does not start below 450 °C. A minimum at 540 °C is followed by a strong increase of resistivity which starts about 100 °C below the phase boundary. The initial value of resistivity after quenching from 700 °C (■ in Fig. 2) is met exactly at the same temperature, indicating again the good quenching procedure. As a difference to the equiatomic alloy the resistivity continues to increase above the phase boundary at about 685 °C (Refs. 2 and 3) though at a much smaller rate. This can be interpreted as an influence of decreasing SRO. In this case an increasing degree of SRO leads to a decrease of resistivity. This could also account for the slight decrease of resistivity at 200 °C in that the resistivity curve tries to meet the SRO equilibrium curve (dash-dotted curve in Fig. 2).

The reversed isochrone behaves in a similar way as for the equiatomic alloy. It is obvious that for 70 at. % Pt the LRO effects on resistivity are much weaker than for 50 at. % Pt. Again a test by isothermal annealing at 650 °C showed that the rising part of the isochrone indeed represents equilibrium states of LRO (see inset of Fig. 2).

Figure 3 gives the isochronal behavior of the Cu-rich alloy. A picture significantly different from the previous alloys is seen: SRO effects dominate the resistivity change. An increase of resistivity is observed above 350 °C up to a maximum at 460 °C which is due to developing SRO. At the maximum the SRO equilibrium line is met and at higher temperatures the resistivity smoothly decreases indicating the destruction of SRO. Note that here SRO leads to an increase in resistivity with an increasing degree of SRO in contrast to the Pt-rich alloy. At 700 °C the value for the initial quench (■ in Fig. 3) is met, indicating again the good reproducibility of the quenching procedure. The reversed isochrone runs back

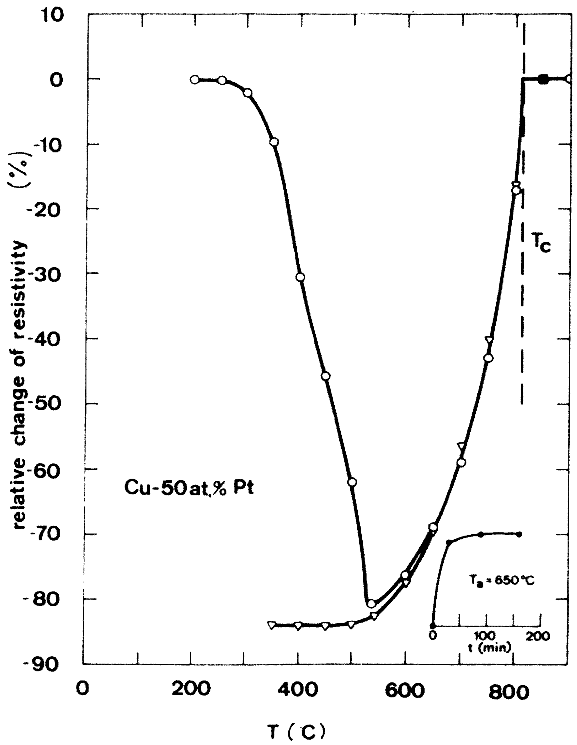

FIG. 1. Isochronal annealing of Cu–50 at. % Pt. The relative change of resistivity $\Delta\rho/\rho_0$ is plotted as a function of annealing temperature. $\Delta T = 50$ °C, $\Delta t = 20$ min. ρ_0 refers to the preannealed state. Inset: isothermal annealing at 650 °C. ○, rising temperatures; ▽, falling temperatures (reversed isochrone); ■, initial value after preannealing and quench.

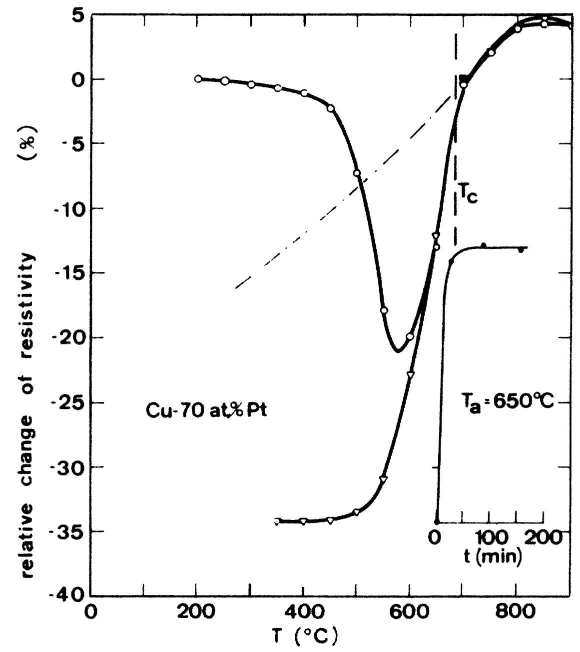

FIG. 2. Isochronal annealing of Cu–70 at. % Pt. The relative change of resistivity $\Delta\rho/\rho_0$ is shown as a function of annealing temperature. $\Delta T = 50$ °C, $\Delta t = 20$ min. ρ_0 refers to the preannealed state. Inset: isothermal annealing at 650 °C. Dash-dotted line: hypothetical SRO equilibrium curve. ○, rising temperatures; ▽, falling temperatures (reversed isochrone); ■, initial value after preannealing and quench.

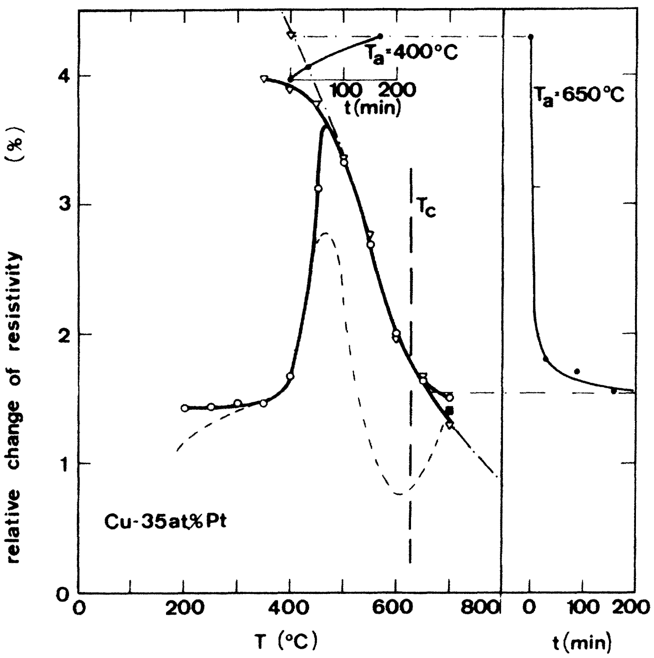

FIG. 3. Isochronal annealing of Cu–35 at. % Pt. The relative change of resistivity $\Delta\rho/\rho_0$ is plotted vs the annealing temperature. $\Delta T = 50$ °C, $\Delta t = 20$ min. ρ_0 refers to the cold-rolled state before the preannealing treatment. Insets: isothermal annealing at 400 and 650 °C. Dash-dotted line: extrapolated SRO equilibrium line. Dashed line: isochronal annealing (first run) after a $\frac{1}{2}$-h 820 °C anneal following the initial cold rolling for sample preparation. ○, rising temperatures; ∇, falling temperatures (reversed isochrone); ■, initial value after preannealing and quench.

on the same line until 460 °C where the atomic mobility becomes too small and the equilibrium line is left. An isothermal anneal at 400 °C shows how the equilibrium line runs (see upper inset of Fig. 3). An isothermal anneal at 650 °C confirms the equilibrium values at higher temperature (lower inset). Note that the phase boundary is crossed without any influence from LRO. The absence of LRO is attributed to the short annealing times (20 min) and the thermal history of the sample.

That the thermal pretreatment is crucial for the observed results can be seen from the dashed line in Fig. 3 which represents another isochrone. Here the sample was annealed very briefly at 820 °C directly after the initial cold rolling for the sample preparation. An increase of resistivity due to SRO is seen at low temperatures. However, at 450 °C the resistivity starts to drop until the phase boundary is reached. At even higher temperatures the resistivity increases again until it reaches the SRO equilibrium line. This behavior can be attributed to the development of LRO in competition to SRO where LRO leads to a reduction of resistivity. The drastic decrease of resistivity during an isothermal anneal at 500 °C by more than 15% (not shown here) indeed gives evidence for the establishment of LRO under these special circumstances. The reversed isochrone behaves as the isochrone and shows no LRO effects.

One should comment upon the fact that SRO leads to a resistivity increase for Cu-rich alloys and to a decrease for Pt-rich alloys. For many systems the sign of the resistivity change can be connected to the number of conduction electrons in the alloy.[6,7] Low electron concentrations lead to resistivity decreases with SRO and vice versa. As the electron concentration increases from Pt to Cu this alloy obeys this simple rule.

Recently SRO in Cu-Pt has been investigated theoretically by calculating electronic properties using the embedded-cluster method based on the Korringa-Kohn-Rostoker coherent-potential-approximation (KKR-CPA) method.[8] An extension of this method to the electrical resistivity might clarify the resistivity behavior due to SRO.

IV. CONCLUSIONS

We have the following conclusions.

(i) Cu–50 at. % Pt and Cu–70 at. % Pt: Approaching the critical temperature from below, disordering processes lead to equilibrium states for certain temperatures.

(ii) Cu–35 at. % Pt: A repeated change between SRO behavior and LRO formation is observed, which depends strongly on the pretreatment of the sample.

(iii) One can conclude that the resistivity measurement technique as used here is suitable to investigate the complicated behavior of simultaneously occurring SRO and LRO and the influence of mechanical and thermal treatment on ordering processes.

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