

ORDER-DISORDER TRANSITION IN CuPt-ALLOYS, INVESTIGATED BY RESISTIVITY MEASUREMENT

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INTRODUCTION

It is evident that ordering effects are essentially dependent on temperature. The formation of long-range order (LRO) in most cases 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.

Effects of short-range order (SRO) frequently are investigated far above a phase boundary, the degree of order continuously decreasing with increasing temperature. Because of rather small differences in the atomic arrangements the formation of these effects is much faster, though equally reflecting the atomic mobility (1).

The effect of SRO on the electronic structure of CuPt-alloys has been calculated by means of the KKR-CPA and the embedded cluster method (2) and it is hoped that the calculations can be extended to the electrical resistivity.

It was the aim of the present work to observe the formation of LRO and SRO in CuPt-alloys by measuring changes in the electrical resistivity during isochronal and isothermal annealing.

EXPERIMENTAL

Cu-alloys with 29,35,50 and 70 at% Pt were induction melted from 99.999 Cu and 99.99 Pt by Degussa.

Foils of about 0.2 mm thickness were rolled with several intermediate anneals in purified Argon atmosphere. Then serpentine shaped samples were cut out of the foils by spark erosion.

Before the isochronal annealing procedure the samples were homogenized just above the phase boundary and quenched into water of room temperature.

The resistivity measurements were made by usual potentiometric method in a bath of liquid nitrogen relative to a dummy specimen. The measuring accuracy was about $\pm 5 \times 10^{-5}$, but the accuracy of the results obviously is limited by the reproducibility of the annealing temperature of about $\pm 2^\circ\text{C}$. Therefore the accuracy for the alloys investigated is given by the resistivity change per temperature interval to: $\pm 5 \times 10^{-4}$ for Cu-29at%Pt and Cu-35at%Pt, $\pm 4 \times 10^{-3}$ for Cu-70at%Pt and $\pm 1 \times 10^{-2}$ for Cu-50at%Pt.

RESULTS AND DISCUSSION

Cu-alloy with 50 at% Pt

In fig. 1 the change of electrical resistivity of Cu-50at%Pt is plotted

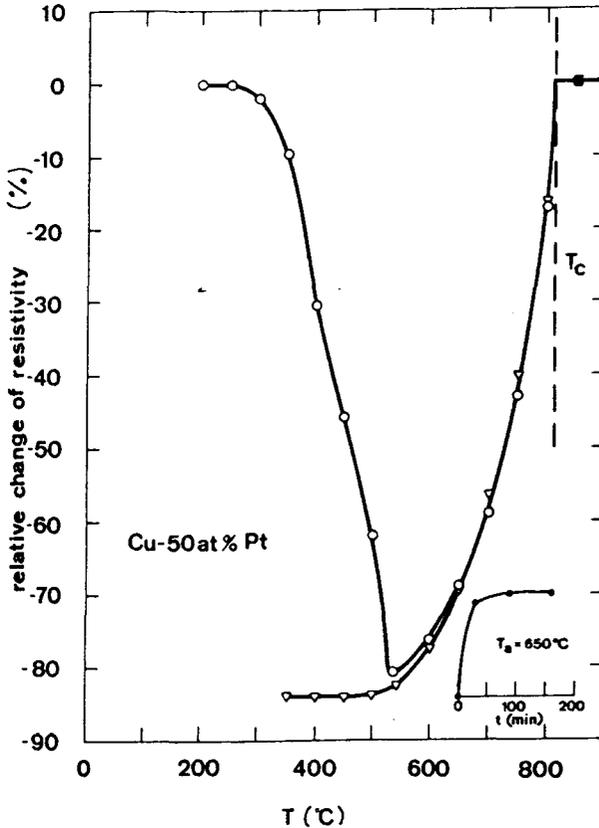


FIGURE 1. Isochronal annealing of Cu-50at%Pt. \circ rising ∇ falling temperature; \blacksquare starting value. Insert: isothermal annealing at 650°C.

versus the annealing temperature. At about 250°C a drastic decrease of resistivity by 80% obviously indicates the formation of LRO. After a minimum at 540°C, where the equilibrium degree of SRO is reached within the isochronal time interval of about 20 min., the resistivity increases again, which must be connected with the beginning destruction of LRO. It is particularly interesting that this effect of disordering starts almost 300°C below the critical temperature at 827°C. Above the critical temperature no measurable change of resistivity was detected.

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 whether the increasing values of resistivity between 540°C and the critical temperature are equilibrium values reflecting the dependence of the LRO parameter has been checked by an isothermal annealing experiment at 650°C: the change of electrical resistivity with annealing time (see inset of fig. 1) shows that a stable state is adjusted.

The results of isochronal annealing for this alloy are in good correspondence with an investigation by Torfs et al. (3).

Cu-alloy with 70at%Pt

Fig.2 gives the change in electrical resistivity of Cu-70at%Pt as a function of the annealing temperature. There starts a slight decrease of resistivity already at 200°C, but the drastic drop of about 20%, which obviously indicates the formation of LRO, starts above 400°C. A minimum at 580°C ($=T_c - 100^\circ\text{C}$) is followed by a strong increase of resistivity.

As a difference to Cu-50at%Pt for this alloy the resistivity continues to increase above the phase boundary at about 685°C, though at a smaller rate. This can be interpreted by a decreasing degree of SRO with increasing temperature, if an increase of SRO means a decrease of the resistivity in this case. This could also account for the slight decrease of resistivity of the present sample at rather low temperatures.

A test by isothermal annealing at 650°C demonstrates the stability of the resistivity values of the increasing part of the isochronal curve (see inset of fig.2).

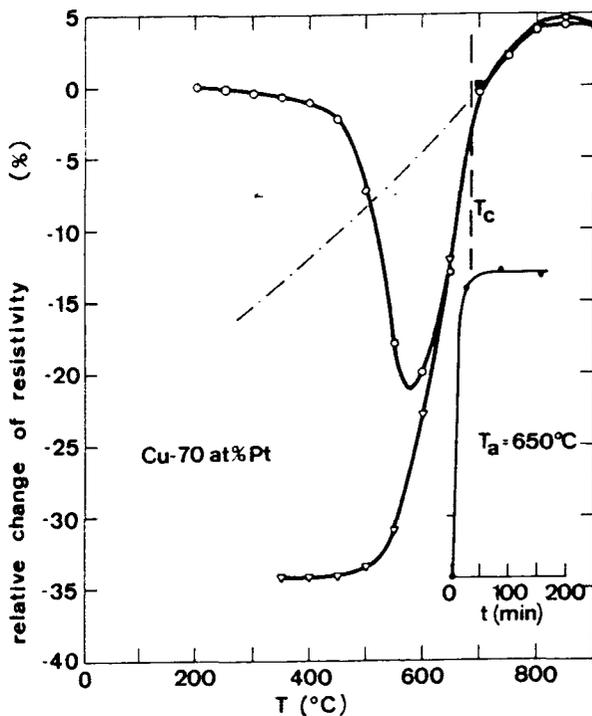


FIGURE 2. Isochronal annealing of Cu-70at%Pt. \circ rising ∇ falling temperature; \blacksquare starting value. Inset: isothermal annealing at 650°C. Dash-dotted: hypothetical SRO-equilibrium line.

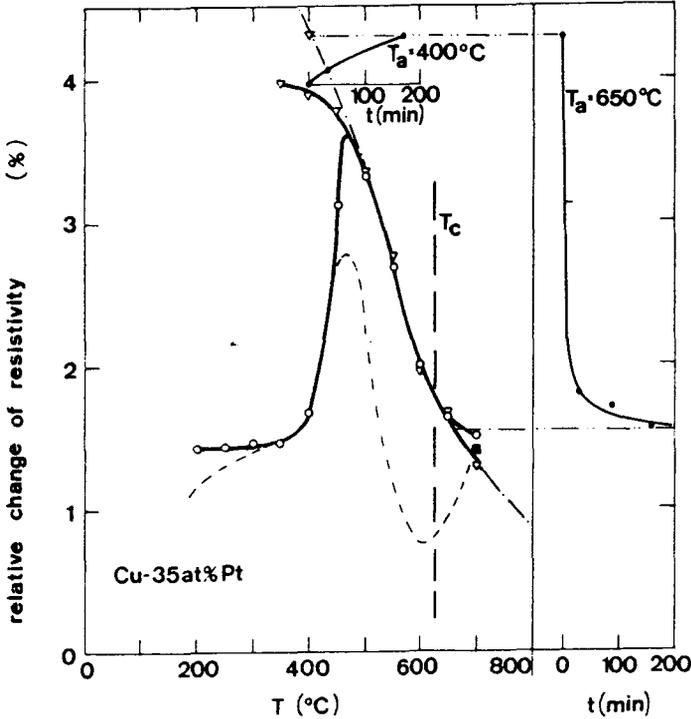


FIGURE 3. Isochronal annealing of Cu-35at%Pt. \circ rising ∇ falling temperature; \blacksquare starting value. Inserts: isothermal annealing at 400°C and 650°C. Dashed line: previous run.

Cu-alloy with 35 and 29 at%Pt

Fig. 3 gives the change of electrical resistivity of Cu-35at%Pt versus annealing temperature during the isochronal annealing experiment. Here the resistivity first **increases** up to a maximum value at 460°C and then **decreases** in a reproducible way (isochrone and reversed isochrone). This can be interpreted by an increase of SRO below 460°C, which in this case increases the electrical resistivity. At the maximum the resistivity equilibrium line is met leading to a decrease of resistivity with decreasing degree of SRO. Note that the equilibrium line crosses the phase boundary at 625°C unchanged. An isothermal annealing experiment at 400°C and 650°C shows the stability of these SRO-equilibrium states (see inset of fig. 3). The absence of LRO is attributed

to the short annealing times (20 min.) and the pretreatment of the sample.

That the thermal history is crucial for the observed result shows the dashed line in fig. 3, which represents another isochrone of the same sample. Here, after a short annealing at 820°C immediately following the initial cold-rolling for the sample preparation, an influence of LRO was observed above 450°C by a resistivity drop below the phase boundary. This interpretation was checked by an isothermal anneal at 500°C (not shown here) yielding a drastic decrease of resistivity by more than 15%.

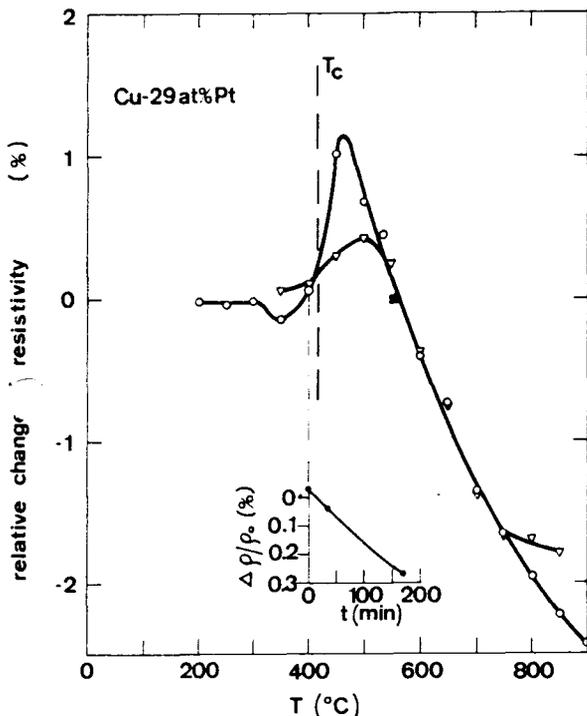


FIGURE 4. Isochronal annealing of Cu-29at%Pt. \circ rising ∇ falling temperature; \blacksquare starting value. Insert: isothermal annealing at 650°C.

Fig. 4 shows that a very similar behaviour was observed for the Cu-29at%Pt alloy. After a first small decrease of resistivity between 300°C and 350°C the resistivity increases up to a maximum at 460°C just above the phase boundary at about 400°C. Then the resistivity decreases until quenching effects are observed above about 750°C. This can be interpreted as increasing and decreasing SRO, where an increase of SRO is accompanied by an increase of resistivity.

The reversed isochrone coincides with the isochrone at rising temperatures above 550°C (equilibrium line). At temperatures near the phase boundary a decrease of resistivity hints at an influence of LRO-formation. This was checked by an isothermal annealing at 400°C: a steady decrease of resistivity confirms this presumption. Therefore the small decrease of resistivity at the beginning of isochronal annealing (350°C) also may be attributed to LRO-effects.

CONCLUSIONS

- i) Cu-50,70 at%Pt: Both alloys show a prompt and strong formation of LRO. The destruction of order starts far below the critical temperature and equilibrium states are achieved for certain temperatures. Effects of SRO only were observed for the alloy with 70at%Pt leading to a decrease of resistivity with increasing SRO.
- ii) The results for the Cu-35at%Pt and the Cu-29at%Pt alloys show a repeated change between SRO-behaviour and LRO-formation depending on the thermal treatment of the sample. In this case an increasing degree of SRO increases the electrical resistivity.
- iii) SRO seems to form independently of LRO and not to be a pre-stage of LRO.

REFERENCES

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