Changes in Electrical Resistivity during Continuous Heating of Cu-13at.%Pt Alloys Quenched from Various Temperatures

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Abstract

The changes in electrical resistivity during continuous heating of Cu-13at.%Pt alloys with $L1_2$ type structure, annealed at various temperatures and immediately quenched, are carefully examined and the relationships between the residual resistivity and the temperature coefficient of resistivity and the order parameter deduced from differential scanning calorimetory are experimentally investigated. The results are compared with those for Cu_3Pd alloys with the same ordered structure, previously reported. The electrical measurement reveals that the electrical resistivity increases just below the order-disorder transition temperature in the same way as that of Cu_3Pd alloys, but the relative magnitude of this increase with respect to the total change upon ordering is smaller than in Cu_3Pd alloys. It is also found that the resistivity change during heating deduced from the thermal behaviour using an experimental equation derived here, agrees sufficiently well with the results of measurement.

Key Words: Cu-13at.%Pdt alloy, Intermetallic compounds, Electrical resistivity, Order-disorder transformation.

1. Introduction

It is well known that the electrical resistivity of the superlattice alloys decreases upon transformation from a disordered to an ordered structure with decreasing temperature [1,2,3]. This is ascribed to the fact that the residual resistivity decreases with increasing relaxation time as the periodicity of the arrangement of the component atoms increases upon ordering [4,5]. However, the temperature coefficient of electrical resistivity increases with increasing order in many alloys [6,7]. Thus, it is possible in some alloys that in a partially ordered state at high temperature, the increase in electrical resistivity owing to a larger temperature coefficient becomes larger than the decrease in the residual resistivity with ordering. One of these alloys is the Cu_3Pd alloy with the $L1_2$ type structure, the electrical resistivity of which increases just below the order-disorder transition temperature (T_c), showing a sharp peak just below T_c on the heating resistivity curve [8]. The present author has demonstrated for this alloy that an experimental equation obtained from relationships between the residual resistivity and the temperature coefficient and the order parameter represents the increase in resistivity just below T_c [9,10]. It has also been found that such behaviour of the resistivity change never appears if the following condition is not satisfied: the temperature coefficient in the ordered state must not only be

larger than in disordered state, but also the residual resistivity must be more sensitive than the temperature coefficient to the order parameter. The Cu_3Pt alloy with the same order structure shows the same behaviour of resistivity change as that in the Cu_3Pd alloy at a composition lower than 15at.%Pt. The relative magnitude of the increase in resistivity just below T_c to total resistivity change with ordering increases as Pt concentration decreases but the total resistivity change decreases. As a result, the increase in resistivity just below T_c is maximum at approximately 13at.%Pt.

The aim of the present investigation was to measure the electrical resistivity of Cu-13at.%Pt alloys obtained in various ordered states after annealing at various temperatures, and to perform differential scanning calorimetry of each sample to deduce the order parameter from the endothermic and exothermic peaks of the DSC curve obtained. It was also our purpose to examine whether or not relationships between the residual resistivity and temperature coefficient and the order parameter similar to those in the Cu_3Pd alloys are observed. Furthermore, the heating resistivity curves deduced from the derived experimental equation were compared with the results obtained directly by resistivity measurement.

2. Experimental Procedures

The Cu-13at.%Pt alloy was prepared by arc melting copper and platinum of 99.99% purity in an argon atmosphere. The alloy ingot obtained was rolled to a thickness of about 5 mm at room temperature and then homogenized at 1170 K for 21.6 ks in an evacuated sealed quartz tube. All the samples were annealed at various temperatures below and above T_c in sealed quartz tubes, and then immediately quenched by releasing the tubes into water.

The electrical resistivity of samples, with a width of about 2 mm, a thickness of about 0.2 mm and lengths of 60-70 mm, was measured by the d.c. four-point method from room temperature to a higher temperature above T_c. The heating rate and sampling time for the measurements were 5 K min^{-1} and 5-10 s, respectively. The differential scanning calorimeter (DSC) measurement of each sample, with a weight of 0.2-0.3 g, was performed with a Seiko SDM5500 DSC 300 instrument at a heating rate of 5 K min^{-1} in a high-purity nitrogen atmosphere, using platinum as the reference material.

3. Results and Discussion

3.1. *Heating electrical resistivity curves of samples annealed at various temperatures*

Figure 1 shows the changes in electrical resistivity of samples in various ordered states induced by annealing at various temperatures during continuous heating at 5 Kmin^{-1}, where the resistivity ratio, that is, the ratio of electrical resistivity to that at T_c (about 1000 K) is taken as

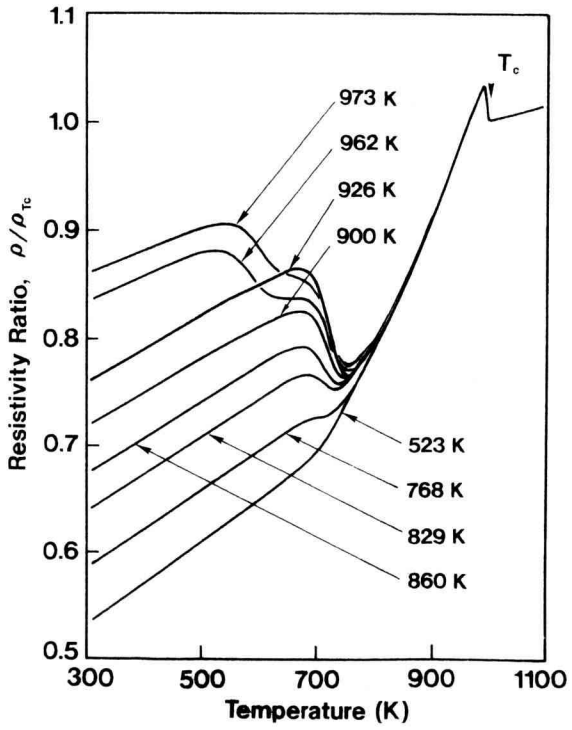

Figure 1. Heating resistivity ratio curves of Cu-13at.%Pt alloy samples prepared by annealing at various temperatures and immediately quenching, where the resistivity ratio is the ratio of electrical resistivity at a given temperature to that at T_c.

the longitudinal axis to avoid any influence of uncertainty in the sample size. The temperature assigned to each curve in this figure is the effective quenching (EQ) temperature, depicting a temperature at which the ordered state of each sample is frozen by successful quenching [10].

It is shown in this figure that the resistivity ratio of all samples increases linearly with temperature below about 500 K and above T_c. It is also seen here that the value of the resistivity ratio near room temperature increases and the slope of the straight part below 500 K decreases with increasing EQ temperature. Above about 800 K, however, the resistivity change of all samples is almost the same, and just below T_c a sharp peak is formed in the heating resistivity ratio curve. Such behaviour just below T_c is very similar to that observed in the Cu_3Pd alloys [9]. However, in samples with EQ temperatures of 973 K and 962 K (being in almost disordered states), the resistivity ratio decreases in two stages, different from the case of the Cu_3Pd alloys. This is ascribed to the fact that the ordering of disordered Cu_3Pt alloy occurring in the first stage promoted by migration of excess vacancies frozen in and in the second stage by migration of equilibrium vacancies [11]. In the Cu_3Pt alloy, the influence of excess vacancies on the ordering of disordered samples is more marked than that in Cu_3Pd alloys, because the higher quenching temperature required for disordering of the Cu_3Pt alloy, which has a higher T_c than the Cu_3Pd alloy, results in higher concentration of the excess vacancy frozen in.

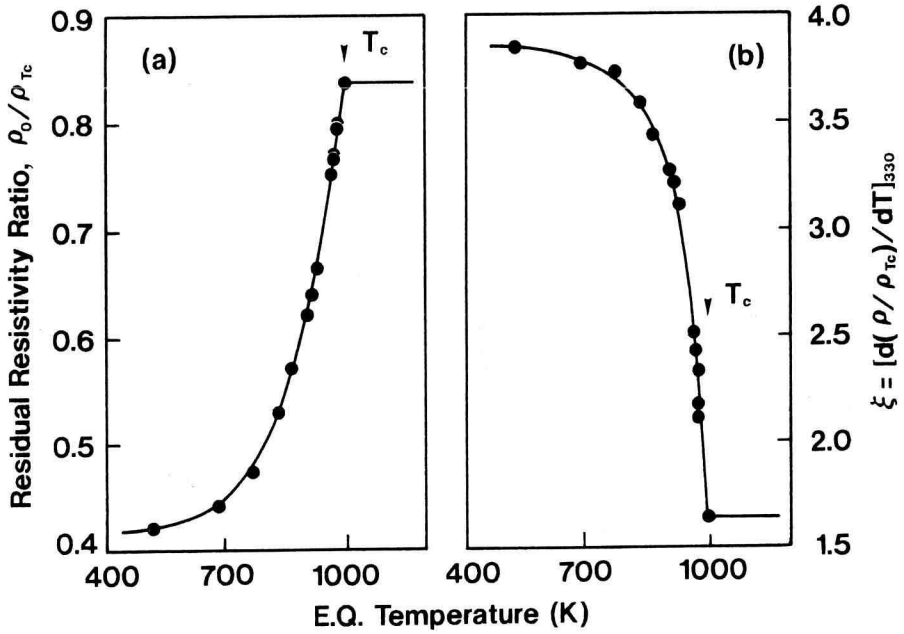

Figure 2. Changes in (a) residual resistivity ratio and (b) temperature coefficient with increasing EQ temperature, showing the temperature at which the ordered state of each sample is frozen by successful quenching.

3.2. *Changes in residual resistivity and temperature coefficient with EQ temperature*

Figure 2 shows changes in the residual resistivity and the temperature coefficient near 330K with EQ temperature. In (a) the residual resistivity ratio ρ_0/ρ_{Tc}, determined by extrapolating the straight part of each curve near 330 K to 0 K in figure 1, is plotted against the EQ temperature and in (b) the temperature coefficient of the resistivity ratio $\xi = [(d\rho/\rho_{Tc})/dT]_{330}$ obtained from the slope of the straight part of each curve near 330 K in figure 1, is plotted against the EQ temperature. The true

value of the residual resistivity ratio is considered to be slightly larger than the value obtained here because of the linear relation between the electrical resistivity and T^5 near 0 K. Also, in the present investigation, a complete disordered sample cannot be obtained because in the plate and bulk samples, some ordering occurs during quenching from temperatures higher than T_c , because of the migration of excess vacancies toward sinks during quenching. Fortunately, as the behaviour of the resistivity change of all samples above T_c is almost the same and increases linearly, the values of the residual resistivity ratio can be determined by extrapolating the straight part of the resistivity ratio curve above T_c, and the temperature coefficient can also be determined from the slope of the straight part within the range of permissible error.

It is evident from figure 2 (a) that no small sharp peak just below T_c, such as that in figure 1, is formed and that ρ_0/ρ_{Tc} essentially decreases with decreasing temperature. It is shown in figure 2 (b) that ξ decreases gradually at lower temperatures and then decreases markedly near T_c. Taking into account the fact that the degree of long-range order in superlattice alloys exhibits a temperature dependence similar to ξ upon the temperature [5,12], these changes are considered to take place due to a decrease in the degree of long-range order with increasing EQ temperature [13].

3.3. *Relationships between ρ_0/ρ_{Tc} and ξ and order parameter*

In order to clarify the relationships between ρ_0/ρ_{Tc} and ξ and the degree of long-range order, $\log [\rho_0(0)/\rho_{Tc} - \rho_0(S)/\rho_{Tc}]$ is plotted against $\log S$ in figure 3(a) and $\log [\xi(S) - \xi(0)]$ is plotted against $\log S$ in figure 3 (b). Here, S is the order parameter depicting the degree of long-range order, obtained from

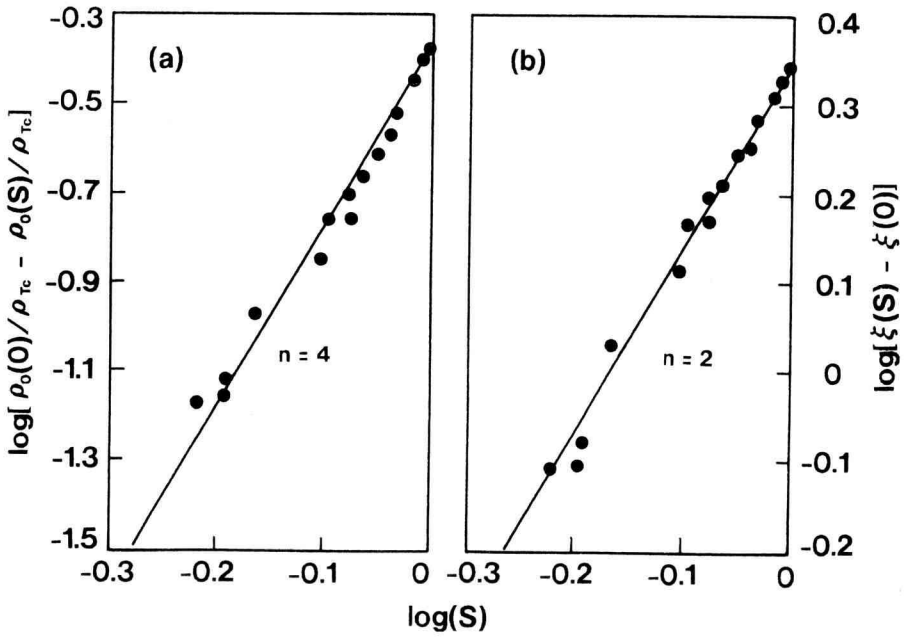

Figure 3. Relationships between (a) $\log [\rho_0(0)/\rho_{Tc} - \rho_0(S)/\rho_{Tc}]$ and (b) $\log [\xi(S) - \xi(0)]$ and $\log S$. The value of n is the slope of each straight line drawn in (a) and (b)

the data of DSC measurement using the method reported previously (10), $\rho_0(0)/\rho_{Tc}$ is the value of ρ_0/ρ_{Tc} at $S = 0$, $\rho_0(S)/\rho_{Tc}$ is the value of ρ_0/ρ_{Tc} at S = any value, and $\xi(0)$ and $\xi(S)$ are the value of ξ at S =0 and any values, respectively.

It is apparent in both figures 3(a) and 3(b) that a straight line can be drawn through the solid circles plotted, although data scattering tends to increase with decreasing S. This implies that relations of both $\log [\rho_0(0)/\rho_{Tc} - \rho_0(S)/\rho_{Tc}]$ and $\log [\xi(S) - \xi(0)]$ with $\log S$ are approximately linear. Thus, since the slope n of the straight line is about 4 in (a) and about 2 in (b), ρ_0/ρ_{Tc} in this alloy can be considered to decrease linearly with increasing S^4, and ξ can be considered to increase linearly with increasing S^2. This indicates that the relationships between ρ_0/ρ_{Tc} and ξ and S in the present alloy exhibit the same tendency as that in the Cu_3Pd alloy, that is, the residual resistivity is more sensitive than the temperature coefficient to the order parameter. However, the slope n = 4 for the residual resistivity is smaller than the slope n = 4.8 in the case of the Cu-13at.%Pd alloy [9].

3.4. *Heating resistivity ratio curves deduced from data of thermal measurement using the experimental equation*

As has previously been reported, the resistivity ratio in ordered alloys such as Cu_3Pd and Cu_3Pt can be described by the following equation [9],

$$\rho_0/\rho_{Tc} = \rho_0(S)/\rho_{Tc} + \xi(S)T. \qquad (1)$$

Also, if the relationships approximated in figure 3 are accepted here, then when values of $\rho_0(0)/\rho_{Tc}$ and $\rho_0(1)/\rho_{Tc}$ are obtained from figure 2(a), and values of $\xi(0)$ and $\xi(1)$ are obtained from figure 2(b), the residual resistivity term and the temperature coefficient term in equation (1) can be obtained by

$$\rho_0/\rho_{Tc} = \rho_0(0)/\rho_{Tc} - (\rho_0(0)/\rho_{Tc} - \rho_0(1)/\rho_{Tc})S^4 = 0.837 - 0.42S^4, \qquad (2)$$

$$\xi = \xi(0) + (\xi(1) - \xi(0))S^2 = (1.64 + 2.19S^2) \times 10^{-4}. \qquad (3)$$

Then, if the value of S at any temperature during continuous heating for each sample can be obtained, we can deduce heating resistivity ratio curves using the following final equation obtained by substituting equations (2) and (3) into equation (1):

$$\rho_0/\rho_{Tc} = 0.837 - 0.42S(T)^4 + (1.64 + 2.19S(T)^2)T \times 10^{-4}. \qquad (4)$$

Changes in S of sample with EQ temperature of 523 K, 860 K and 973 K during heating, obtained from the area of endothermic and exothermic peaks of DSC curves, are shown in figure 4. The curves indicated by solid, half-filled and open circles correspond to samples with EQ temperature of 523K, 860 K and 973 K, respectively.

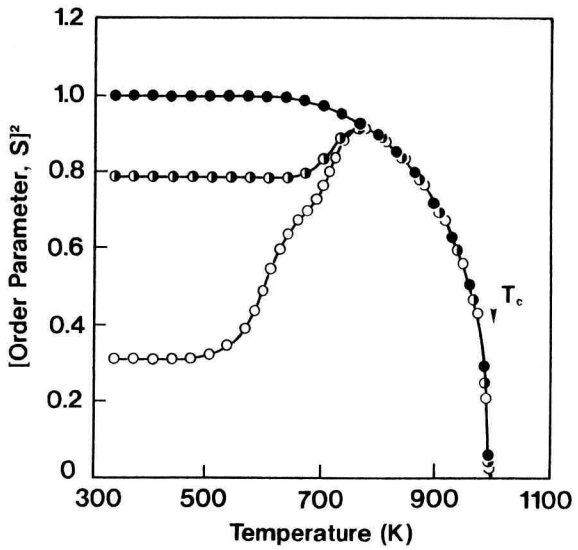

Figure 4. Changes in S during continuous heating of samples annealed at various temperatures and then quenched, deduced from data of thermal measurement. Solid, half-filled and open circles correspond to the samples with EQ temperature of 523 K, 860 K and 973 K, respectively.

It is seen here that in the samples annealed at the higher temperatures the order parameter increases and then begins to

decrease with increasing temperature because the low degree of long-range order attained increases in the first stage of heating. The increase in S of the highly disordered sample with EQ temperature of 973 K takes place in two stages corresponding to the two exothermic peaks in the DSC curve, which implies the occurrence of the two stages of ordering promoted by the migration of excess vacancies and equilibrium vacancies [11].

We can now deduce heating resistivity ratio curves of these three samples using the changes in S during heating in figure 4. The results calculated using equation (4) are shown in figure 5. The narrow solid lines in this figure show results obtained by electrical resistivity measurement for each sample, circles and lines show the results obtained by calculation and the solid, half-filled and open circles have same meaning as in figure 4.

All calculated curves represent the increase in the resistivity ratio just below T_c although the magnitude of the peak formed by this increase is slightly lower than that of the resistivity measurement indicated by the narrow line. It is also evident for samples with EQ temperature of 860 K and 523 K that, except for the fact that the value of the calculated resistivity ratio is slightly higher than the narrow line between about 650 K and about 750 K, the calculated curves are in excellent agreement with experimental curves. In the sample with EQ temperature of 973 K, it is seen that the calculated resistivity ratio is slightly higher than the narrow line from room temperature to about 650 K but becomes lower than the narrow line above 650 K, and as a result, the step change in the resistivity ratio corresponding to the two stages of ordering becomes more moderate than that shown by the narrow line.

Also, the temperature at which the narrow line begins to decrease is lower than that in the calculated results. This may be ascribed to a slight difference between the concentration of excess vacancies frozen in of the bulk sample for DSC measurement and that of the plate sample for resistivity measurement. It has previously been reported that which of the two stages of ordering is predominant depends on the sample size, where a difference in size rises to the difference of the concentration of excess vacancies frozen in [11].

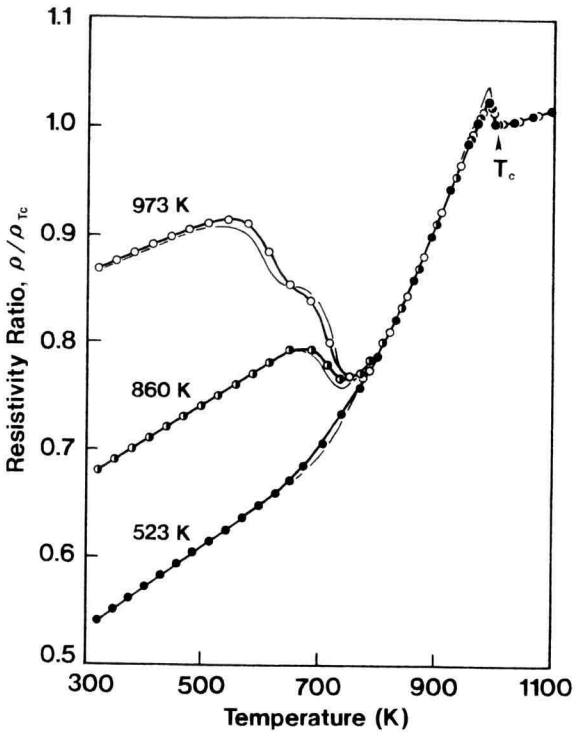

Figure 5. Comparison between heating resistivity ratio curves calculated using equation (4) from values of S in figure 4 and results of measurement. Narrow solid lines show results of measurement and solid, half-filled and open circles have the same meanings as in figure 4.

4. Conclusions

The electrical resistivity change during continuous heating of Cu-13at.%Pt alloys annealed at various temperatures and then quenched was examined and the relationships between the residual resistivity and the temperature coefficient and the order parameter obtained by DSC measurement were investigated. Also, the heating resistivity curves deduced from the derived experimental equation were compared with the results

obtained directly by resistivity measurement. The following conclusions are drawn.

(1) The increase in resistivity ratio just below T_c similar to that occurring in Cu_3Pd alloys is observed in all samples of Cu-13at.%Pt alloys annealed at various temperatures. However, the relative magnitude of the increase with respect to the amount of resistivity change due to ordering is considerably lower than that in Cu-13at.%Pd alloy.

(2) The residual resistivity ratio decreases with increasing order and this ratio has an approximately linear relationship to S^4, while the temperature coefficient has an approximately linear relationship to the second power of S.

(3) The heating resistivity ratio curves calculated using an experimental equation obtained from these relation-ships reproduce the sharp peak just below T_c and are generally in good agreement with the results of electrical measurement.

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