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Letter

Electrical resistance change during ordering or disordering in Au_3Cu alloy

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ABSTRACT

The behavior of electrical resistivity of Au_3Cu alloy which shows resistivity increase at first and then decrease during the ordering process, is studied by means of the isothermal annealing method. The annealing time of the resistivity maximum on the isothermal curve measured at the annealing temperature is longer than that of the maximum on the curve measured at liquid nitrogen temperature which is different from the predicted result by Aubauer [1]. Therefore, Aubauer's explanation is not applicable at least for the abnormal resistivity change during the ordering of Au_3Cu alloy.

1. Introduction

A structural ordering of atoms in many alloys has been usually studied by X-ray and electron diffraction experiments [2,3] and by the electrical resistivity measurements [4–8]. Normally the resistivity of alloys has to decrease for better periodicity of atomic ordering with increase of the ordering degree. However, the isothermal annealing curves of the resistivity of some alloys show abnormal increases and then decreases during ordering [8]. In the Au_3Cu alloy, the resistivity increases, also, in the early stage and then decrease during the isothermal annealing [6]. The many diffraction studies have showed that in this alloy the ordering of the atoms proceeds during the isothermal annealing. Aubauer [1] showed by calculation that the resistivity maximum should take place during the isothermal annealing when the mean free path of conduction electrons coincides with the ordered domain size.

In the present experiment, the electrical resistances of the Au_3Cu alloy are measured at the annealing and liquid nitrogen temperature during ordering or disordering. The results can be used to check the validity of the calculation by Aubauer [1], because the mean free path of the conduction electrons increases clearly with the temperature decrease.

2. Experimental

The Au_3Cu alloy was prepared by welding 3 times in a carbon crucible in vacuum from Au and Cu metals which were purchased from Tanaka Kikinzoku Kogyo Corp. and Johnson Matthey Chemicals Ltd., respectively. Nominal purities of the materials were 99.99% pure and 99.999% pure for Au and Cu, respectively. The alloy lump was cold-rolled to thin foils (30–35 μm in thickness) and cut to strip of width about 1 mm.

The foil specimens were spot-welded with Pt current and potential leads and pre-annealed in vacuum for 5 h at 1073 K to reduce the dislocation density. After the pre-annealing the specimen was cooled down to room temperature in the furnace. The specimen was set in a tube of quartz glass which enclosed argon gas after the setting, and annealed in a furnace. A thermo-couple of type K was set near the specimen in the tube. To reduce the effect of some ordering due to furnace cooling after the pre-annealing the order and disorder treatments were repeated a few times. The electrical resistance was measured at the high temperature (for example about 503.2 K, 453.2 K, 423.2 K etc.) during the annealing and measured also at the liquid nitrogen temperature. In each time, the tube was quickly pulled out from the furnace and put into the liquid nitrogen. Therefore, the resistance was measured at the same structural condition as it is at the high temperature. The resistance measurement was done by standard four probe method.

3. Results and discussions

The phase diagram of Au–Cu alloy shows that the order phase is stable below around 463 K for the Au_3Cu alloy [9]. Therefore, for the ordering treatment in Fig. 1, a temperature 453.2 K was chosen as the annealing temperature. We cannot get the perfect ordering within a reasonable experimental duration because the temperature is too low. Therefore the annealing for ordering was stopped at some duration in the 453.2 K isotherm. The initial degree of ordering depends on the duration and is not the same for the curves in Fig. 1 at immediately before starting the annealing. The same specimen is used in the present investigation for easier comparison after various heat treatments. The resistance at 453.2 K immediately after each ordering treatment is shown at the position of 0 min annealing time, respectively. The values differ from one another mainly due to the difference of the annealing time at 453.2 K. The behavior of resistance curve except early part would not largely change by the degree of ordering. The isothermal resistance curves measured at each annealing temperature are shown in Fig. 1 for 503.2 K, 483.2 K, 473.2 K and 463.2 K. The measured resistance dur-

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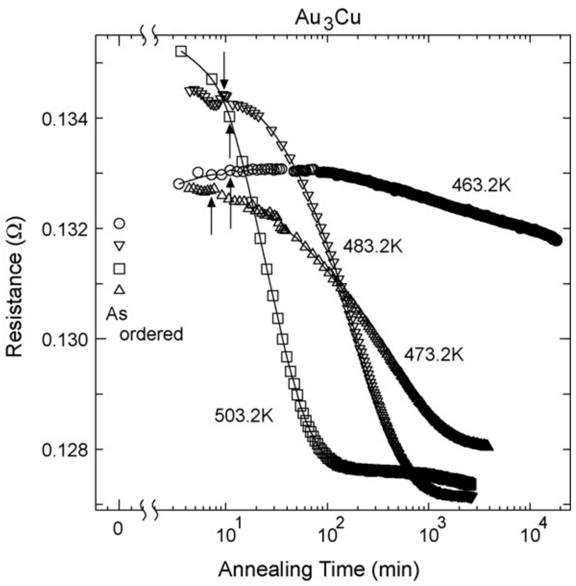

Fig. 1. Isothermal resistance curves measured at various annealing temperatures (T_A) after various ordering treatments at 453.2 K. Each curve starts from the temperature about (T_A−5 K) during the heating up to each annealing temperature. The resistance values at 453.2 K immediately after the ordering treatment are shown at 0 min for each curve with the same mark, respectively. The annealing temperature was attained at the position of arrow in each curve. Annealing time at 453.2 K for the ordering; 503.2 K curve: about 40.4 days, 483.2 K curve: 26.7 days, 473.2 K curve: 1.6 days, 463.2 K curve: 20.1 days.

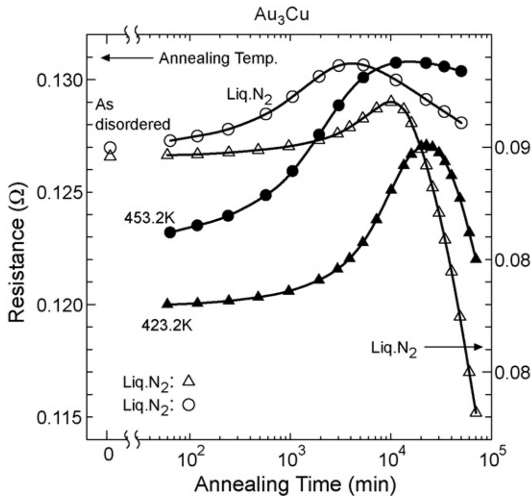

Fig. 2. Isothermal resistance curves measured at various annealing temperatures and at liquid nitrogen temperature after disordering treatment at 503.2 K. Full and open marks of each pair show the data of the same annealing measured at annealing and liquid nitrogen temperature, respectively. Annealing time at 503.2 K for the disordering; 453.2 K curve: about 3000 min, 423.2 K curve: 3900 min.

ing heating up is shown in Fig. 1 from below 5 K of the annealing temperatures. Each specimen temperature arrived to the annealing temperature at an arrow on each curve. The specimen is annealed at 453.2 K for 1.6–40.4 days before each annealing as described in the figure caption. As shown later in Fig. 3, the resistance maximums are observed in all curves at 453.2 K isotherm after the disorder treatments. As mentioned before, the temperature of phase boundary between the order phase and mixed phase is around 463 K for Au_3Cu alloy [9] and the resistance curve of the specimen in disorder state shows the resistance maximum during ordering [6]. With these ordering treatments at 453.2 K annealing, the resistances increase to some levels around the maximum. Therefore, as shown in Fig. 1, at the annealing above 473.2 K after ordering treatment, the resistance decreases with the progress of the disordering. The disordering progresses faster at higher annealing temperature. The resistance decrease begins before reaching up to the desired annealing temperature except the case of 463.2 K annealing. Some scatterings of data points in the early parts of curves are caused by temperature fluctuation to control to a constant temperature. On the isothermal curve at 463.2 K the resistance decreases more slowly due to small difference from the temperature of ordering at 453.2 K and due to low annealing temperature. The resistance differences around at the starting points of the curves are mainly caused by temperature dependence of resistances and are caused partially by the difference of the degree of ordering.

As observed in Fig. 1, about 200 min time period is needed to reach to the disordered state at 503.2 K. After annealing at 503.2 K for 3000–3900 min (these times are sufficient enough for the disordering treatment because these are over 10 times longer than 200 min), the specimen was annealed isothermally at various temperatures (423.2 K and 453.2 K). The results are shown in Fig. 2 for the resistance curves measured at each annealing temperature and at liquid nitrogen temperature. Full and open marks of each pair show the data at annealing and liquid nitrogen temperature, respectively. The plots at 0 min show values for “as disordered” by annealing at 503.2 K. Each curve has resistance maximum without exception. Furthermore, the resistance curves measured at liquid nitrogen temperature have the maximums at shorter annealing time than those at the annealing temperature. The crystallographic structures at liquid nitrogen temperature must be the same to those of at the annealing temperature because the specimen is fast cooled to liquid nitrogen temperature. To show the curves in the same figure for comparing of the position of maximum, the *y*-axis for the curves at liquid nitrogen temperature is shifted against to it at the annealing temperature. The maximum resistance positions of curves appear at shorter annealing time for higher annealing temperature (compare with 453.2 K curve and 423.2 K curve). Higher rate of ordering at higher annealing temperature is easily understood because the ordering in Au_3Cu alloy would take place by vacancy diffusion [6]. As already mentioned before, difference at beginning parts between the curves is mainly caused by the annealing temperature difference because the resistance is measured at different temperature. Partly it is caused by different degrees of disordering because the electrical resistance at the initial state of annealing is not the same even at the liquid nitrogen temperature. At 423.2 K annealing, sharp decrease after the resistance maximum in both curves would be caused by higher number density of ordered domains at lower annealing temperature.

As the result in Fig. 1, the temperatures above 473.2 K are used for disordering treatment. The resistance curves during the ordering are shown in Fig. 3, in which the annealing temperature is the same though the temperatures of the disordering treatment are different among them (473.2 K, 483.2 K and 503.2 K). As one can see in Fig. 1, each annealing curve at the temperature above 473.2 K shows resistance decrease to a certain value in a certain annealing time. Therefore, as shown in Fig. 3, the maximum annealing time was chosen so that it is longer than the disordering period at each temperature. The data at 0 min show as disordered values by annealing (473.2–503.2 K). Differences between the curves are caused by the different ordering degrees. Each curve has, also, the resistance maximum during annealing. Furthermore, the resistance curves measured at liquid nitrogen temperature have, also, the maximums at shorter annealing time than those at the annealing temperatures. Slower appearance of the resistance maximum on the curve disordered at higher temperature is caused by higher disordering degree at the beginning.

From the facts described above, it can be concluded that the resistance maximums appear at shorter annealing times for the

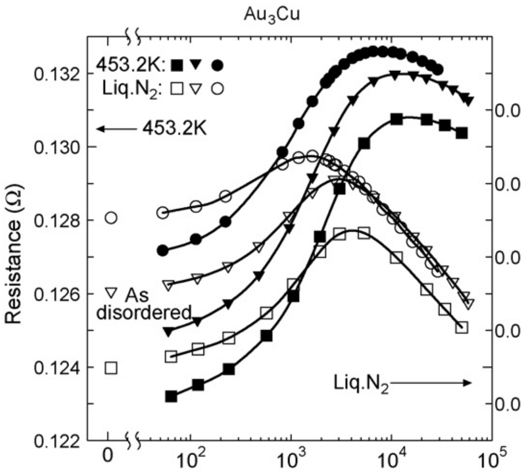

Fig. 3. Isothermal resistance curves measured at 453.2 K and at liquid nitrogen temperature after various disordering treatments. The disordering temperature is different from one another (503.2 K, 483.2 K and 473.2 K). Full and open marks of each pair show the data at annealing and liquid nitrogen temperature, respectively. Disordering conditions: (■, □) at 503.2 K for approximately 3000 min; (▼, ▽) at 483.2 K for 2700 min; (●, ○) at 473.2 K for 4600 min. The resistance at liquid nitrogen temperature immediately after the disorder treatment (resistance at 0 min.) differs from one another. This fact shows the differences of the degree of order.

measurements at liquid nitrogen temperature even though the orderings start from various disorder levels and the orderings occur at different temperatures.

Aubauer [1] predicted theoretically such a resistivity maximum occurs during the ordering. In Aubauer's theory, the resistivity maximum during the annealing appears when the mean free path of the conduction electron is the same order to the size of ordered domain.

According to Aubauer's theory, the resistivity maximum on the curve measured at liquid nitrogen temperature has to be observed at longer annealing time than that of the curve at the annealing temperature. As mentioned before, the mean free path at liquid nitrogen temperature (lower temperature) is longer than that at the annealing temperature (higher temperature). The ratio between the resistance at 453.2 K and that at liquid nitrogen temperature is about 1.4 at around each maximum of the curve. Therefore, at least, the mean free path at liquid nitrogen temperature must be 1.4 times longer there. If we follow Aubauer's calculation, the size of ordered domain at liquid nitrogen temperature is 1.4 times larger than the size at annealing temperature, though the size must be the same at both temperatures. We can conclude, at least, that Aubauer's explanation is not applicable for the resistivity maximum of annealing curve during the ordering on the Au_3Cu alloy.

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