Reversion Phenomenon in Cu-Ti Alloy*

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The reversion phenomenon of Cu-3.17wt% Ti alloy was investigated, with special attention to the reversion process of side band structure, by means of electrical resistivity measurements, X-ray diffraction, hardness and tensile tests, and transmission electron microscopy. The temperature ranges of aging and reversion were 300~500°C and 350~700°C, respectively.

Analysis of the electrical resistivity change shows the reversion process to be described by a first order rate equation. The activation energy for reversion was about 2.3 eV.

A reversion phenomenon is also observed in the mechanical properties and microstructure.

From the results of X-ray diffraction experiment, the reversion process of side band structure in this alloy is explained with a zone complex model with diffused periodicities.

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I. Introduction

Cu-Ti alloy is a well known age-hardenable alloy and a considerable amount of work^{(1)~(18)} has been done on its aging characteristics.

Recently, with more than about 1 wt% Ti, this alloy has been reported to show the side bands in Debye-Scherrer patterns under suitable aging conditions⁽⁴⁾⁽⁵⁾⁽¹⁰⁾⁽¹²⁾⁽¹³⁾⁽¹⁷⁾⁽³¹⁾, which suggests that a modulated structure by spinodal decomposition in this system may be anticipated.

Tsujimoto et al.⁽¹⁵⁾⁽¹⁶⁾ have recently reported the results of X-ray small angle scattering experiments that the initial aging process of a Cu-4 wt% Ti alloy proceeds in a mode of spinodal decomposition and its critical temperature was estimated to be between 320 and 350°C. Tsujimoto et al.⁽¹⁷⁾ and Miyazaki et al.⁽¹²⁾⁽¹³⁾ investigated also in detail the side band structure and the mechanism of precipitation process of the alloy.

However, very few reports have been published on the reversion phenomenon in this alloy. Zwicker⁽⁵⁾ described that hardness and electrical resistivity changes of the alloy induced at the

initial stage of aging at low temperatures (300 and 375°C) are completely reverted by heating at 725°C for 30 sec.

In the present study, the reversion phenomenon in connection with thermal stability of the side band structure of this alloy is investigated in detail. The kinetics and the mechanism of reversion are also discussed.

II. Specimens and Experimental Procedures

Specimens were prepared from a commercial Cu-25 wt% Ti mother alloy and electrolytic copper. The alloys were melted in graphite crucibles under argon atmosphere with a high frequency induction furnace and cast into a permanent mold. After intermediate annealing at 800°C for 1 hr, 1 mm ϕ wire and 1 mm thick ribbon were prepared by drawing and rolling. Ti contents of the specimens were 3.17 and 1.17 wt%. The 3.17 wt% Ti alloy was mainly used for reversion experiments.

Solution treatment was performed at 950°C for 1.5 hr, followed by quenching into iced water. Specimens were sealed in quartz tubes evacuated and filled with argon gas containing 5% H₂ in order to prevent oxidation of specimens and sublimation of titanium. Quartz tubes were crushed in water immediately after quenching.

The reversion process was investigated mainly by means of electrical resistivity measurements and X-ray diffraction. In some cases, micro Vickers hardness and tensile tests were also performed. The 1 mm ϕ wire specimen was used

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for potentiometric measurement of the electrical resistivity. Two voltage terminals of the same material as the specimen were spot-welded to the specimen with a separation of about 14 cm. The measurement was performed in liquid nitrogen. The specimens for X-ray diffraction were cut from 1 mm thick sheets. The profile change of (200) line was measured using FeK_α radiation mainly by a diffractometer with scintillation counter. In some cases, Debye-Scherrer photographs were taken with CuK_α radiation from about 0.4 mm ϕ wire specimens thinned with nitric acid. The profile change was measured by a micro-photometer.

In the aging treatment, the specimens were sealed in pyrex tubes filled with argon gas except for short time aging. In the reversion treatment, all the specimens were heated directly in heating medium, because of very short time of heating (second order).

Structural changes due to reversion were investigated by transmission electron microscopy. About 0.15 mm thick sheets were electropolished by both Bollmann and window methods in phosphoric acid solution saturated with CrO_3 .

III. Experimental Results

Figure 1 shows the copper side of the Cu-Ti equilibrium phase diagram⁽¹⁹⁾. The figures in brackets indicate the solid solubility of Ti in copper and the composition of specimens.

1. Electrical resistivity change during reversion

Figure 2 shows the resistivity changes during isothermal reversion at temperatures between 350 and 450°C, after aging at 300°C for 25 hr. The aging conditions were so selected that a modulated structure was expected to appear during aging. The electrical resistivity first increases up to $\Delta\rho_{\max}$ due to the redissolution of the decomposed phase and then decreases by the decomposition due to aging at the reversion temperature. As shown in the figure, for a constant aging condition, the amount of reversion increases and the time to reach $\Delta\rho_{\max}$ becomes shorter with increasing reversion temperature. These relations are tabulated in

Fig. 1 Solid solubility of Ti in copper.

Fig. 2 Electrical resistivity change during reversion after 300°C x 25 hr aging.

Specimen: Cu-3.17 wt % Ti alloy.

Table 1.

The reversion process may be described by a first order reaction,

$$1 - f = \exp(-Kt), \quad (1)$$

Table 1 Numerical relation between the apparent amount of reversion and reversion time, after aging at 300°C for 25hr.

300°C x 25 hr aging		
	Apparent amount of reversion* (%)	Reversion time** (sec)
500°C reversion	≈37	<5
450°C reversion	≈33	<5
425°C reversion	≈18	≈15
400°C reversion	≈24	≈40
375°C reversion	≈11	≈160
350°C reversion	≈6	≈420

* Apparent amount of reversion=Increment of electrical resistivity during reversion/Constant decrement of electrical resistivity during aging x 100

** Reversion time=Time required to reach the maximum reversion

where f , t and K are the fractional reaction, the reaction time and the rate constant, respectively. Moreover, the rate constant is given by

$$K = A \exp(-Q/kT), \quad (2)$$

where A is the frequency factor, Q the activation energy for the reaction, T the absolute temperature and k the Boltzmann constant. From the slope of a linear relation between $\ln(1-f)$ and t , the rate constant K is obtained. The Arrhenius plot of eq. (2) also gives the activation energy Q .

Figure 3 shows that the reversion process at and below 400°C shown in Fig. 2 can be described by a first order equation up to f of 0.6 or 0.7. Here f is calculated as $\Delta\rho/\Delta\rho_{\max}$. For a prolonged reversion treatment, some deviation from the

Fig. 3 The first order reaction plot of reversion obtained from Fig. 2.

Fig. 4 Arrhenius plots obtained from the temperature dependence of rate constant K and the initial tangent to the reversion curve.

equation is observed.

Figure 4 shows the Arrhenius plot to obtain the activation energy for the reversion process. The activation energy Q_I obtained from the initial slope of the reversion curves is about 2.3 eV. On the other hand, Q_K obtained from temperature dependence of the rate constant K is about 1.8 eV. The difference between Q_I and Q_K will be discussed in the next chapter.

The resistivity change due to reversion at 500°C was investigated after several aging treatments to give a fixed amount of resistivity decrease. The result is shown in Fig. 5. The amount of reversion decreases with increasing aging temperature. This fact suggests that the precipitate at a higher aging temperature is more stable against a constant reversion treatment.

Figure 6 shows the relation between the aging

Fig. 5 Electrical resistivity change during reversion at 500°C after a constant resistivity decrease by aging under the indicated conditions.

Specimen: Cu-3.17 wt% Ti alloy.

Fig. 6 Electrical resistivity change during reversion at 450°C after aging at 300°C for various periods. Specimen: Cu-3.17 wt% Ti alloy.

time at 300°C and the amount of reversion at 450°C. The amount of reversion increases with aging time, but after reaching the maximum it seems to decrease a little due to the coarsening of precipitates after prolonged aging, which is the same tendency as observed in Cu-Cr alloy⁽³²⁾⁽³³⁾. It must be pointed out that the resistivity increase was not observed in the specimen aged at 300°C for 10 min. Such a behavior may be expected in a specimen aged for a very short time, which has only a small amount of decomposed phase and therefore has a large contribution of resistivity decrease due to decomposition at the reversion temperature.

Repetition of reversion similar to those observed in other age-hardenable alloys also occurs in this alloy. Figure 7 shows such a resistivity change during a cyclic thermal treatment; 300°C × 25 hr aging and 700°C × 5 sec reversion. The resistivity after the first and the second reversion are a little higher than that obtained immediately after quenching. This result indicates that some fast decomposition reaction proceeds even during the rapid quenching from the solution treatment temperature. The formation of clusters during quenching in this alloy has been confirmed by the present authors⁽²⁰⁾.

2. Change in mechanical properties during reversion

Figure 8(a) shows the hardness change in a specimen aged at 500°C for 30 sec, followed by reversion at 600°C. The resistivity change under

Fig. 7 Cyclic change of electrical resistivity during aging and reversion.
Specimen: Cu-3.17 wt % Ti alloy.

Fig. 8 Comparison of hardness and resistivity change during reversion.
Specimen: Cu-3.17 wt % Ti alloy.

the same condition is shown in Fig. 8(b). A slight decrease in hardness is observed during reversion. Figure 9(a) shows the hardness during repetition of reversion, under the same condition as that in Fig. 7. The reversion of hardness appears to be incomplete as compared with that in the resistivity. On the contrary, the 0.2% proof stress and the tensile strength revert almost completely during repetition of reversion as shown in Fig. 9(b). The discrepancy may be due to the difference in the thermal effects between the thin wire and the thick disk specimens. The specimen size for the hardness test was about 15 × 15 × 1 mm, while that for the resistivity measurement and the tensile test was 1 mmφ. The former was too massive to be heated up to the reversion temperature of 700°C in such a short time as 5 sec. By a longer reversion treatment, its hardness was nearly fully reverted as shown by a chain line in Fig. 9(a).

Fig. 9 Change of 0.2% proof stress, tensile strength and hardness during a cyclic thermal treatment of aging and reversion.
Specimen: Cu-3.17 wt % Ti alloy.

Fig. 10 Change of profiles of X-ray diffraction lines by aging and reversion.
Specimen: Cu-3.17 wt% Ti alloy.

3. Results of X-ray diffraction

Figure 10 shows the change in diffraction profile induced by the reversion treatment. The profile of (200) line obtained from a specimen aged at 450°C for 1 hr is characterized by the appearance of asymmetric side bands. The side band intensity in the high angle side is stronger than that in the low angle side, and the peak position of the former is somewhat nearer to the main line. After the reversion treatment at 700°C for 10 sec, these side band peaks disappear and only a sharp main diffraction line remains. Similarly, a very diffuse (420) line from an aged specimen changes to more sharp doublet lines after reversion.

Figure 11 shows the change in I/I_0 during reversion; I/I_0 being a ratio of the intensity of side band to that of main line, which is obtained from the profile of (200) line. I_H and I_L in the figure mean the intensities of the high angle and low angle side bands, respectively. The specimen was aged at 400°C for 1 hr and reverted at 550°C. Both intensities of the side bands decrease up to the reversion time of about 20 sec.

Fig. 11 Change of intensity of side bands during reversion at 550°C after 450°C x 1 hr aging.
Specimen: Cu-3.17 wt% Ti alloy.

This result is in good agreement with the resistivity change indicated in Fig. 12.

Figure 13 shows the changes in peak position of the side bands and in the main diffraction line during reversion. The Bragg angle difference between side bands decreases during reversion as observed in the case of aging. The peak position in the high angle side is hardly shifted, but that in the low angle side approaches the main diffraction peak position during the reversion process.

4. Structural change by reversion

Photograph 1 shows the structure of a 3.17 wt% Ti specimen aged at 450°C for 25 hr. Characteristic tweed-like contrasts are due to the precipitates of the intermediate phase grown from side band structure. By heating at 700°C for 10 sec, the precipitates are dissolved almost perfectly and a nearly homogeneous matrix is obtained as shown in Photo. 2. Here, it must be mentioned that in this case the resistivity change was completely reverted and the diffraction pattern of the intermediate phase disappeared.

Fig. 12 Change of electrical resistivity during reversion under the same condition as in Fig. 11.

Fig. 13 Changes in peak position of side bands and main (200) line during reversion at 550°C after 450°C × 1 hr aging.

Specimen: Cu-3.17 wt% Ti alloy.

Photographs 3 and 4 show the structure of a 1.17 wt% Ti alloy specimen after the same heat treatments as above. The precipitate observed in Photo. 3 is a discrete plate perpendicular to $\langle 100 \rangle$ of the matrix. Moreover, precipitates on dislocations, precipitate-free zones around dislocations and the interfacial dislocations introduced by the loss of coherency are observed. The precipitates disappear almost entirely after reversion.

The above results show that the precipitates grown up from the side band structure after a prolonged aging are also unstable thermally.

IV. Discussion

In Cu-Ti alloys, side bands have been observed at a relatively early stage of aging at temperatures between 350 and 500°C. In the present investigation, the aging temperature was chosen between 300 and 500°C, and the reversion temperature was from 350 up to 700°C.

Recently, Tsujimoto et al.⁽¹⁵⁾ have concluded the critical temperature T_c of spinodal decomposition in a Cu-4 wt% Ti alloy to be about 320~350°C by X-ray small angle scattering experiments. The decomposition process at temperatures lower than T_c proceeds in a mode of spinodal decomposition in the initial stage, and gradually transforms into the growth process of normal precipitates expressed by the Porod approximation⁽²¹⁾. For example, the aging

condition for the spinodal decomposition is reported⁽¹⁵⁾ to be within about 4 min at 260°C.

Photo. 1 Transmission electron micrograph of the characteristic tweed-like precipitates after aging at 450°C for 25 hr.

Specimen: Cu-3.17 wt% Ti alloy.

Photo. 2 Transmission electron micrograph of the matrix shown in Photo. 1 after heating at 700°C for 10 sec, which shows nearly complete re-dissolution of precipitates.

Photo. 3 Transmission electron micrograph of discrete plate-like precipitates after aging at 450°C for 25 hr. Specimen: Cu-1.17 wt% Ti alloy.

Photo. 4 Transmission electron micrograph of the matrix shown in Photo. 3 after heating at 700°C for 10 sec.

According to their conclusion, the aging temperature of the present X-ray diffraction experiment, 450°C, is considered to be above the critical temperature, and the aging condition in the electrical resistivity measurement, 300°C $\times$ 25 hr, is outside the region of spinodal decomposition. In the present study, very weak and broad side band peaks are confirmed to exist after 300°C $\times$ 25 hr aging.

1. The reversion kinetics by resistivity measurement

As mentioned above, the reversion behavior measured by electrical resistivity is considered to be due to the reversion of the side-band structure.

As shown in Fig. 3, the reversion kinetics is well represented by a first order reaction, and two different activation energies, 2.3 and 1.8 eV, are obtained. The former Q_i is obtained from the temperature dependence of an initial slope of a reversion curve of resistivity. The latter Q_K is from the temperature dependence of the rate constant K . As mentioned in Chapter III, the resistivity change during reversion is considered to be the sum of an increasing term resulting from re-dissolution and a decreasing one from decomposition. From the shape of resistivity curves during reversion, it may be said that re-dissolution is the main reaction at an initial stage and decomposition, including growth, proceeds at a relatively later stage. Therefore, Q_i is more probable for the activation energy of reversion reaction than Q_K which is obtained under a relatively strong influence of other reactions than the redissolution inevitable in the present reversion experiment.

The activation energy for the impurity diffusion of Ti in Cu has not been obtained, but the values for Fe and Co, the same transition elements as Ti, are given as 2.2⁽²²⁾ and 2.3 eV⁽²²⁾, respectively. The activation energy for the impurity diffusion of Ti in Cu would be supposed to be not greatly different from these values. Hence, it may be that Q_i is nearly equal to the activation energy for the impurity diffusion of Ti in Cu. For the reason mentioned above, the initial stage of the reversion in the side band structure of Cu-3.17 wt % Ti alloy seems to be rate-controlled by the diffusion of Ti in the Cu matrix.

2. The change in mechanical properties during reversion

The mechanical properties, such as hardness, proof stress and tensile strength, decrease during reversion. As will be discussed later, the results of X-ray diffraction experiment show that the amplitudes of the concentration distribution of Ti in the side band structure decrease during reversion. The above fact and the disappearance of some precipitates due to reversion as shown in the microphotographs (Photos. 1~4), can be regarded as providing evidence for the reduction of mechanical properties by reversion.

3. The results of X-ray diffraction experiments

As the explanation of side band diffraction effects, various models have been proposed^{(10)(23)~(30)}. Tsujimoto et al.⁽¹⁸⁾ have recently proposed a model, in which zone complexes as shown in Fig. 14(a) are considered to be distributed with diffused periodicities. They have succeeded in explaining qualitatively the asymmetries of position and intensity of side bands and, moreover, their shifting to the main peak during aging.

The Tsujimoto model⁽¹⁸⁾ is as follows: As shown in Fig. 14(a), a_0 , a_1 and a_2 are lattice parameters of the matrix, Ti-rich and Ti-poor regions, respectively. c_0 , c_1 and c_2 are the Ti concentration in these regions. $2b_1$ and $2b_2$ are the numbers of lattice planes in the Ti-rich and Ti-poor zones. The broken line shown in Fig. 14(b) is the scattering intensity function $I_Z(s)$ from the zone complex. The peak position, the peak intensity and the half width of $I_Z(s)$ are

shown in the figure, where f_0 is the scattering factor of a lattice plane. The chain line is the diffraction function $I_p(s)$ due to diffused periodicities. The peak position of $I_p(s)$ is situated at $h/a_0 \pm 1/\bar{Q}a_0$ of a reciprocal lattice, where $\bar{Q}a_0$ is the most probable distance between the zone complexes. The shape of $I_p(s)$ depends upon the diffuseness of periodicity in the distribution of the zone complexes. The actual scattered intensity observed is the product of both functions and is shown by a full line.

Especially the asymmetric positions of side bands are difficult to be explained by other models^{(23)~(27)} with a constant periodicity considering only the modulations of solute atom concentration and lattice parameter. These asymmetric positions can also be explained by the three-phase model^{(28)~(30)} with random distribution. However, their shifting to the main peak during aging is difficult to be explained by this model. Therefore, the Tsujimoto model⁽¹⁸⁾ is considered by the present authors to be most

probable for the aging process of the side band structure in this alloy.

So far as the results of the present reversion experiment are concerned, the behavior seems to be also explained by the re-dissolution of such zone complexes distributed at random. However, the distribution of zone complexes at the start of reversion must be the same as that at the end of aging. Therefore, a qualitative interpretation of the reversion process observed in the present experiment will be offered using the Tsujimoto model.

The results of the present X-ray diffraction experiments may be summarized as follows:

(1) Both I_H/I_0 and I_L/I_0 , and the peak intensities of side bands decrease during reversion at first and increase thereafter by the contribution of precipitation.

(2) The low angle side band approaches rapidly the main peak during reversion, but the high angle one and the main peak are hardly shifted during both reversion and later precipitation. (See Fig. 13)

(3) The side bands become broad during reversion.

It is generally supposed that the shape and position of the $I_p(s)$ change to some extent during the re-dissolution of small zone complexes, but it is always symmetry around the main peak. As the reversion process can be considered to be mainly a thinning process of a central zone at least at an initial stage, it is expected that the position of side bands is decided mainly by that of $I_Z(s)$, because no remarkable changes in the position and shape of the function $I_p(s)$ are expected.

Therefore, the result (2) that the peak positions of the high angle side band and the main diffraction line were hardly shifted is considered to correspond to the fact that the peak positions h/a_2 of $I_Z(s)$ on high angle side and h/a_0 of the main diffraction line were not shifted. The above consideration suggests that Ti concentrations of the Ti-poor zone c_2 and the matrix c_0 remain nearly constant during reversion.

On the contrary, the result (2) that the peak position of the low angle side band approached rapidly the main peak corresponds to the fact that the peak position h/a_1 of $I_Z(s)$ approaches h/a_0 due to the decrease in a_1 . Therefore, the height of Ti-rich zone in the center of zone

Fig. 14(a) Schematic diagram of a zone complex for side band structure.

(b) Schematic explanation of the side band effect by the distribution of zone complexes with diffused periodicities.

(c) A proposed model of the reversion process of the side band structure in Cu-Ti alloy.

complex shown in Fig. 14(a) decreases during reversion.

The result (1) that the peak intensity of the high angle side band decreased during reversion at an early stage corresponds to the decrease in peak height $(2b_2f_0)^2$ of $I_Z(s)$, which is introduced by the decrease in b_2 . Therefore, the width of Ti-poor zone shown in Fig. 14(a) is narrowed. The decrease in b_2 also causes the broadening of $I_Z(s)$ due to the increase in half width $1/a_2b_2$. A similar result that the peak intensity of low angle side band decreased and the shape became broad also corresponds to the decrease in b_1 .

From the above considerations, the reversion process of the side band structure observed in this alloy can be interpreted as follows: During reversion, both the width and Ti concentration of the Ti-rich zone decrease, while the Ti concentration of Ti-poor zone is nearly constant and the width becomes narrower from its inner side by the supply of Ti atoms from the Ti-rich central zone. It appears that the distance between the periodical zone complexes hardly change during the reversion at least at an initial stage. The schematic diagram of the reversion process in this alloy is shown in Fig. 14(c).

It must be noticed that the spacing between side bands is similarly reduced during both reversion and aging, but the behavior during reversion results from the change in the Ti concentration of a central zone and that during aging is a result of the increase in the spacing between zone complexes with diffused periodicities. Furthermore, during both aging and reversion processes, the low angle side band became broader than the high angle one and the peak height of the former was always lower than that of the latter. This suggests that the width of Ti-rich zone is always considerably smaller than that of the Ti-poor zone.

V. Summary

The reversion of Cu-3.17 wt% Ti alloy was investigated by various experimental methods with special attention to the reversion process of the side band structure. The main results obtained are summarized as follows:

(1) The reversion process investigated by electrical resistivity measurements is described

by a first order rate equation up to fractional reaction f of 0.6 or 0.7.

(2) The activation energy for reversion obtained from the initial slope of the resistivity reversion curves is about 2.3 eV, which is nearly equal to the activation energy for the impurity diffusion of Ti in Cu.

(3) The reversion phenomena are also observed in the mechanical properties.

(4) For the explanation of the results of X-ray diffraction, the following reversion model for the side band structure in this alloy is proposed:

Zone complexes with diffused periodicities are distributed after aging. During reversion treatment, both the width and the concentration of the Ti-rich zone decrease, but the concentration of Ti-poor zone remains nearly constant and the width becomes narrower by the supply of Ti atoms from the adjacent Ti-rich zone. The most probable distance between such zone complexes does not seem to change so much during reversion.

(5) The structure change during reversion can be observed by transmission electron microscopy. The precipitates in a later stage of aging, which are not considered to be the side band structure but an intermediate phase, can also revert.

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