Formation of Titanium Hydride in Dilute Cu–Ti Alloy by Aging in Hydrogen Atmosphere and Its Effects on Electrical and Mechanical Properties

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We have investigated the specific contributions of titanium-hydride precipitates to the improvement of electrical conductivity and strength for Cu–0.36 mol% Ti alloys aged in a hydrogen atmosphere at 773 K, where Cu4Ti phase is not to appear. During the aging, titanium-hydride particles, which have a composition of H/Ti = 2, are formed by reaction of solute titanium with hydrogen diffused into the alloy. The particles have an octahedral shape with facets parallel to {111} of the matrix. The size and volume fraction of the hydride particles increase with aging time, and then level off after aging for 100 h, while the number density exhibits a maximum at 24 h. The precipitation reduces the concentration of solute titanium in the matrix and leads to significant improvement of the electrical conductivity, to the level comparable to pure copper. The dispersed TiH₂ particles gives rise to strengthening with the Orowan mechanism, of approximately 40 MPa at a maximum in yield strength.

Keywords: copper–titanium alloy, titanium hydride, precipitation, age-hardening, electrical conductivity

1. Introduction

Cu–Be based alloys are widely used for electronic components such as connectors and lead frames, because of their high strength and high electrical conductivity. Substitutes for the alloys are sought after, however, as beryllium is potentially toxic and is also one of the rare elements. Age-hardenable Cu–Ti alloys are being considered as a candidate. While these alloys are attractive in that their mechanical strength is comparable to that of Cu–Be alloys, their electrical conductivity is inferior to that of the Cu–Be alloys.¹–⁵ Recently, however, it was found that the electrical conductivity of age-hardenable Cu–Ti alloys could be significantly improved by aging the alloys at 600 to 800 K in a hydrogen atmosphere.¹ ⁵ This has encouraged research and development of high-strength and high-conductivity Cu–Ti alloys for practical applications.⁶–⁹

Figure 1 shows a Cu-rich portion of the Cu–Ti binary phase diagram.¹⁰) When Cu–Ti alloys containing approximately 1 to 6 mol% Ti are solution-treated above 1100 K and subsequently aged at a temperature between 600 and 800 K in a vacuum, the supersaturated solid solution of copper (Al-type, lattice parameter a = 0.361 nm) undergoes spinodal decomposition, and Cu₄Ti (D₁₅, a = 0.584 nm, c = 0.362 nm) is formed in the matrix. On the other hand, if the alloy is aged in a hydrogen atmosphere, precipitation of Cu₄Ti occurs first, similarly to the case of aging in a vacuum, but, in addition, titanium hydride (C₁₁, a = 0.444 nm) forms as a result of the reaction of solute Ti with hydrogen diffused into the alloy. The former promotes the mechanical strength, and the latter improves the electrical conductivity through reduction of The concentration of Ti in the matrix.⁴¹¹¹²

Since the strength and conductivity of Cu–Ti alloys are significantly influenced by precipitation of Cu₄Ti and titanium hydride, in order to improve these properties, it is important to control the amount and the number density of the precipitate particles, as well as the kinetics of precipitation, by adequately choosing the alloy composition and the condition of thermomechanical treatments such as prior-deformation, aging temperature and hydrogen pressure. Precipitation of Cu₄Ti by conventional vacuum-aging and their effects on material properties have already been studied extensively.¹–³ In the recent studies of aging in a hydrogen atmosphere,⁴–⁸,¹³ both Cu₄Ti and titanium hydride phases are formed in alloys containing 1 to 6 mol% Ti, where it was difficult to evaluated contributions of each phase. In this study, in order to provide a basis for understanding, influences of co-precipitation of titanium hydride and its
effects on the electrical and mechanical properties have been investigated. A dilute Cu–Ti alloy was aged in a hydrogen atmosphere at 773 K, where precipitation of Cu$_4$Ti does not occur because of the low Ti concentration, and the formation behavior of titanium hydride and the variation in the concentration of Ti in the matrix were studied directly and indirectly using transmission electron microscopy (TEM), chemical analysis for hydrogen content, and measurements of dc electrical resistivity. In addition, effects of the formation of titanium hydride on the variation of the electrical conductivity and the strength were evaluated and were discussed quantitatively on basis of the precipitation behavior.

2. Experimental Procedures

An ingot of Cu–Ti dilute alloy was prepared by arc-melting pure copper (99.99% in purity) and pure titanium (99.99%) in an argon atmosphere. The chemical composition of the ingot analyzed by Inductively-coupled plasma/atomic emission spectrometry was Cu-(0.36 ± 0.01)mol% Ti. With this composition, Cu$_4$Ti phase must be absent at temperatures above 680 K (see Fig. 1).\textsuperscript{10,14} The ingot was cold rolled down to 0.8 mm thickness, and from this plate strips measuring 25 mm in length and 3 mm in width, and pieces for tensile tests measuring 10 mm in gauge length and 2 mm in width were cut out. The specimens were solution-treated at 1153 K for 20 h in a vacuum and quenched into ice water. The quenched specimens were vacuum-sealed with 3 g of commercial titanium hydride powder, whose composition is TiH$_1$$_92$, in a silica capsule of about 105 mm in length and 10 mm in inner diameter. By maintaining the capsule at 773 K, it is filled with hydrogen released from the titanium hydride. By this procedure, specimens were aged at 773 K in a hydrogen atmosphere and then cooled down to room temperature. The hydrogen pressure in the capsule was estimated to be approximately 0.4 MPa, according to thermodynamic data of titanium hydride reported in the literature.\textsuperscript{15} Some specimens were vacuum-sealed without titanium hydride and were aged at the same temperature for comparison.

The microstructures of the specimens aged in the hydrogen atmosphere were observed by TEM and scanning TEM (STEM). Thin-foil specimens for TEM observations were first ground to less than 80 µm in thickness, then electro-polished in a solution of 10 vol% nitric acid in methanol at 243 K, and finished by low-angle ion milling with an argon ion beam of below 3 kV. A high-purity argon gas (99.9999% pure) was used for the ion source. For TEM and STEM observations, JEOL JEM-2000FX operated at 200 kV and FEI TITAN operated at 300 kV were used, respectively. The hydrogen content of the specimens aged in the hydrogen atmosphere was analyzed by the argon-carrier fusion thermal conductivity method. The electrical resistivity was measured at 293 and 77 K by the using a constant current dc four-terminal technique (current: 10 mA). Vickers hardness was examined with an applied load of 0.5 kgf and a holding time of 10 s. The average hardness was obtained from 12 indentations, excluding the maximum and minimum values. Tensile tests were carried out using a tensile testing machine ORIENTEC U-1872 at room temperature. The initial strain rate was set to $8.3 \times 10^{-4}$ s$^{-1}$.

3. Results

3.1 Hydrogen content

Figure 2 shows the hydrogen contents, $C_{\text{H}}$, in the specimens aged at 773 K in the hydrogen atmosphere. The value of $C_{\text{H}}$ for the as-quenched specimen was less than 0.01 mol%. The $C_{\text{H}}$ value increased with aging time but leveled off at about 100 h, apparently arriving equilibrium. The hydrogen content in the equilibrium state was approximately 0.78 mol%.

3.2 Hydride

Figure 3 shows bright-field (BF) TEM images and selected area electron diffraction (SAD) patterns of the as-quenched specimen (a), and of those aged at 773 K for 24 h (b) and 408 h (c) in the hydrogen atmosphere. The incident beam direction was close to the [001]$_{\text{m}}$ zone axis. Here, the subscript “m” indicates the matrix phase (the copper solid solution). The as-quenched specimen was a single-phase copper solid-solution with some dislocations (Fig. 3(a)). In the SAD pattern, only spots from the face-centered cubic (fcc) structure of the copper solid solution are observed. In the specimen aged for 24 h in the hydrogen atmosphere, rhombic contrasts of approximately 40 nm in size are seen in the matrix (Fig. 3(b)). The SAD pattern shows weak spots assignable to titanium hydride (C1 type, $a = 0.444$ nm), together with those caused by double diffraction,\textsuperscript{5,6} revealing that the rhombic contrasts correspond to titanium hydride particles. The hydride particles coarsened during aging in the hydrogen atmosphere and their average size was about 80 nm after aging for 408 h (Fig. 3(c)).

Figure 4 shows a STEM bright-field image (a) and high-resolution image (b) of the specimen aged at 773 K for 48 h in the hydrogen atmosphere. In both the cases, the incident beam direction is close to the [011]$_{\text{m}}$ zone axis. From observations of the titanium hydride particles from other zone axes, these precipitates are found to have an octahedral shape with rounded corners. The orientation relationship between the matrix and the hydride was (001)$_{\text{m}}$ // (001)$_{\text{p}}$ and

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig2.jpg}
\caption{Hydrogen content in Cu-0.36 mol% Ti alloy aged at 773 K under an estimated hydrogen pressure of 0.4 MPa.}
\end{figure}
Here, the subscript "p" indicates the hydride. The interfaces between the matrix and the hydride are parallel to \{111\}_m and are semi-coherent (the inset of Fig. 4(b)). The misfit strain was estimated to be 0.22 by analyzing the SAD pattern. Misfit dislocations are introduced approximately every 1.2 nm along the interfaces.

Figure 5 shows the average diameter, \( d \), of the titanium hydride particles in the specimens aged at 773 K in the hydrogen atmosphere. The values of \( d \) were obtained by examining 10 to 50 hydride particles in every specimen using TEM: the volume of each particle was estimated first from its dimensional observed, assuming a regular octahedral shape, the average volume of the octahedral particles \( V_{av} \) was computed, and the average diameter was evaluated by taking this volume as that of a sphere (as \( d = \frac{2 \cdot 3}{\pi} \cdot \sqrt[3]{V_{av}} \)). The value of \( d \) was approximately 40 nm before aging time of 24 h, whereas it increased to 80 nm after 48 h and then remained at 80 nm even after 408 h.

### 3.3 Electrical conductivity

Figure 6 shows the electrical resistivity, \( \rho \), at 293 and 77 K of the specimens aged at 773 K in the hydrogen atmosphere and in a vacuum. The electrical resistivity of the as-quenched specimen was 51.9 n\( \Omega \)m at 293 K, which is indicated by the dotted line “a” in Fig. 6, and 32.77 n\( \Omega \)m at 77 K, indicated by the line “b”. The resistivity of the specimens aged at 773 K in a vacuum, data 3 and 4, was almost constant, because no precipitation occurs at this temperature and composition. On the other hand, the resistivity decreased by aging in the hydrogen atmosphere, data 1 and 2, and approached the
values of pure copper, 17.2 n\(\text{m}^3\) at 293 K and 2.2 n\(\text{m}^3\) at 77 K (line “d”). It became almost constant after 100 h.

### 3.4 Strength

Figure 7 shows the Vickers hardness, \(H_v\), of the specimens aged at 773 K in the hydrogen atmosphere and in a vacuum. For comparison, the hardness of Cu–3 mol% Ti alloy aged at the same temperature in the hydrogen atmosphere and in a vacuum is also shown.\(^5\) The hardness of pure copper and solution-treated Cu–0.36 mol% and 3 mol% Ti alloys are indicated by the dashed lines (a, b, c).

The fracture took place with necking for all the specimens. The fracture surface exhibited a typical ductile dimple pattern, indicating no signs of hydrogen embrittlement.
1. The solubility of hydrogen in pure copper at 773 K under a hydrogen pressure of 0.4 MPa is estimated to be $7.1 \times 10^{-4}$ mol\% by Sieverts’ law.\(^\text{10}\) The hydrogen concentration, $C_\text{H}$, of Cu–0.36 mol\% Ti alloy aged in the hydrogen atmosphere was significantly higher than the solubility in pure copper. This is because solute Ti in the copper solid solution reacts with hydrogen to form titanium hydride.\(^\text{4-6}\) The hydrogen concentration in the alloy reached approximately 0.78 mol\% after 100 h. This value is close, within the experimental accuracy, to the hydrogen concentration of 0.72 mol\% corresponding to a H/Ti ratio of 2. The composition of the titanium hydride formed in the copper matrix is therefore approximately $\text{H}/\text{Ti} = 2$.

The volume fraction, $f^{(2)}$, and number density, $n$, of the hydride particles can be estimated from the hydrogen concentration of the specimen $C_\text{H}$ (shown in Fig. 2) and the particle size of the hydride observed by TEM (Fig. 5). Note that they are important parameters for quantitative analysis and evaluation of the electrical conductivity and strength.

We define the numbers of Cu and Ti atoms in the alloy as $M_\text{Cu}$ and $M_\text{Ti}$, respectively, and the number of H atoms dissolved in the alloy as $M_\text{H}$. We assume that all H atoms exist in the hydride phase and that Cu atoms are not soluble in the hydride. In addition, we assume that the composition of the hydride is $\text{H}/\text{Ti} = 2$ from the early stage of precipitation, although it can be in the range from 1.5 to 2.\(^\text{17}\) The validity of this assumption is discussed in the next section. We define the number of Ti atoms in the copper solid solution as $M^{(1)}_\text{Ti}$, that in the hydride as $M^{(2)}_\text{Ti}$, the atomic volume of the copper solid solution as $\Omega^{(1)} = (1.19 \times 10^{-29} \text{m}^3)$, and the volume per chemical unit of the hydride as $\Omega^{(2)} = (2.19 \times 10^{-29} \text{m}^3)$.

The volume fraction of the hydride phase, $f^{(2)}$, is given as

$$f^{(2)} = \frac{M^{(2)}_\text{Ti} \Omega^{(2)}}{(M_\text{Cu} + M^{(1)}_\text{Ti} \Omega^{(1)} + M^{(2)}_\text{Ti} \Omega^{(2)})}$$

(1)

Using the relations $M^{(1)}_\text{Ti} = M_\text{Ti} - M^{(2)}_\text{Ti}$ and $M^{(2)}_\text{Ti} = (1/2) M_\text{H}$, it can be rewritten as

$$f^{(2)} = \frac{1}{2 \frac{M_\text{H}}{M_\text{Cu}}} \left( \frac{M_\text{Ti}}{M_\text{Cu}} - \frac{1}{2} \frac{M_\text{H}}{M_\text{Cu}} \right) \Omega^{(1)} + \frac{1}{2} \frac{M_\text{H}}{M_\text{Cu}} \Omega^{(2)}$$

(2)

In terms of the concentrations of titanium and hydrogen, $C_\text{Ti} = (3.6 \times 10^{-3})$ and $C_\text{H}$, $M^{(1)}_\text{Ti}/M_\text{Cu}$ and $M^{(2)}_\text{H}/M_\text{Cu}$ are expressed as $M^{(1)}_\text{Ti}/M_\text{Cu} = C_\text{Ti}/(1 - C_\text{H})$ and $M^{(2)}_\text{H}/M_\text{Cu} = C_\text{H}/[(1 - C_\text{H})(1 - C_\text{Ti})]$, respectively. The volume fraction $f^{(2)}$ is calculated by eq. (2) as a function of time using the values of $C_\text{H}$ shown in Fig. 2. The result is shown in Fig. 9 by black diamonds. It increased with aging time to reach approximately 0.7% at 100 h.

The number density of the titanium hydride particles, $n$, was estimated by the following procedure. The denominator of eq. (1) is the volume of the alloy, $V$, and the numerator is the volume of the hydride phase. Because the latter can be written as the product of the number of the hydride particles, $N$, and their average volume, $\bar{v}$, the volume fraction can be expressed as $f^{(2)} = N \bar{v}/V$. Therefore, the number density, $n = N/V$

$$n = \frac{f^{(2)}}{\bar{v}}$$

(3)

Figure 9 also shows $n$ calculated from eq. (3) using the values of $\bar{v}$ that were evaluated from TEM observations (shown in Fig. 5 as the diameter of the particles). The number density reached a maximum by aging for 24 h and then decreased as a result of coarsening of the hydride particles.

### 4.2 Amount of solute Ti in the matrix

The amount of solute Ti in the solid-solution matrix can be...
estimated from the electrical resistivity. The following equation holds for the resistivity of the alloy $\rho$, that of the matrix, $\rho(1)$, and that of titanium hydride, $\rho(2)$, assuming that the hydride particles are spherical and randomly dispersed in the matrix:\(^{18}\)

$$f^{1}(\rho(1) - \frac{1}{\rho}) + f^{2}(\frac{1}{\rho(2)} - \frac{1}{\rho}) = 0$$

(4)

Here, $f^{1}$ is the volume fraction of the matrix phase and is equal to $1 - f^{2}$. When $f^{2}$ is small and $\rho(2)$ is much larger than $\rho$, eq. (4) can be solved for $\rho/\rho(2)$:

$$\rho/\rho(2) \cong 1 + 3 f^{2}$$

(5)

The resistivity of TiH$_{1.75}$ has been reported to be 239 n$\Omega$m at 77 K,\(^{19}\) which is more than one order of magnitude higher than that of the solid-solution alloy (Fig. 6). We assume that $\rho(2)$ is of the same order of magnitude. It then follows that $\rho(2) \gg \rho$. The resistivity of the matrix phase, $\rho(1)$, calculated by eq. (5) using the resistivity of the specimen at 77 K, $\rho$ (data 2' in Fig. 6) and the volume fraction of the hydride phase, $f^{2}$ (Fig. 9), turn out virtually equal to $\rho$. This is because $f^{2}$ is almost 0.7 (Fig. 9) so that the contribution of the hydride phase to the resistivity of the specimen, $\rho$, is negligibly small.

The resistivity of the matrix phase, $\rho(1)$, is related to the concentration of solute titanium $C_{Ti}(1)$, according to Nordheim’s rule:

$$\rho(1) = \rho_{Cu} + AC_{Ti}(1)$$

(6)

Here, $\rho_{Cu}$ is the resistivity of pure copper ($\rho_{Cu} = 2.2$ n$\Omega$m at 77 K), and the coefficient, $A$, is 95 $\pm$ 4 n$\Omega$m/mol% Ti dissolved in copper.\(^{12}\) Figure 10 shows the variation of $C_{Ti}(1)$ with aging time calculated from the resistivity (data ‘1’ in Fig. 6) using eq. (6). The concentration of solute Ti in the as-quenched alloy is 0.35 mol% according to eq. (6), which agrees with the result of the chemical analysis, 0.36 mol%. It decreased by aging in the hydrogen atmosphere as titanium hydride was formed. After 100 h it approached zero, attaining an equilibrium. This indicates that the virtually all Ti atoms in the alloy were consumed to precipitation of the hydride.

The concentration of solute Ti in the matrix, $C_{Ti}(1)$, can be calculated also from the hydrogen concentration $C_{H}$ shown in Fig. 2 and the concentration of Ti in the alloy $C_{Ti}$. By expressing the composition of titanium hydride as $H/Ti = x$, it can be written as

$$C_{Ti}(1) = \frac{M_{Ti}^{(1)}}{M_{Cu}^{(1)} + M_{Ti}^{(1)}} = \frac{C_{Ti} - \frac{x}{1 - C_{H}}}{1 - \frac{x}{1 - C_{H}}}$$

(7)

The data labeled ‘2a’ and ‘2b’ in Fig. 10 show $C_{Ti}(1)$ calculated from eq. (7) with $x = 1.5$ and 2, respectively. The latter, 2b, agrees better with data 1 derived from the electrical resistivity. This supported the assumption that the composition of titanium hydride formed by aging in the hydrogen atmosphere is $H/Ti = 2$. That the values of the $C_{Ti}(1)$ of data 2b after 100 h are slightly less than zero must be due to errors in the chemically analysis of $C_{H}$ and/or $C_{Ti}$.

### 4.3 Electrical conductivity

The data of electrical resistivity at 293 K of the Cu–0.36 mol% Ti alloy aged at 773 K in the hydrogen atmosphere and in a vacuum (data 1 and 3 in Fig. 6) have been converted to electrical conductivity and are shown in Fig. 11 (data 1 and 2, respectively). Corresponding data of Cu–3 mol% Ti alloy reported in an earlier paper\(^{30}\) are shown in the same figure (data 3 and 4) for comparison. The conductivity is expressed in % IACS, percentage of International Annealed Copper Standard at 293 K, 5.80 × 10$^{-7}$ m$^{-1}$. The conductivity of the as-quenched Cu–0.36 mol% Ti alloy, 31% IACS, agrees well with the value calculated from eq. (6), 33% IACS. The conductivity does not change by aging in a vacuum (data 2), because the concentration of solute Ti in the matrix does not change. In contrast, by aging in the hydrogen atmosphere the conductivity significantly increases and eventually approaches 100% IACS (data 1), because the concentration of solute Ti in the matrix decreases as titanium hydride forms.

When Cu–3 mol% Ti alloy was aged in a vacuum (data 4 in Fig. 11), the conductivity gradually increased from 5.4% IACS to 18% IACS at 48 h.\(^{32}\) By the aging at 773 K the concentration of Ti in the solid solution is reduced to the solubility limit at this temperature, 0.8 mol%\(^{10,14}\) where the volume fraction of Cu$_{4}$Ti phase is about 10%. The conductivity in the fully aged state may be estimated by adopting the same relation as eq. (5), on the assumption that the resistivity of Cu$_{4}$Ti is much higher than that of the matrix. With the latter, $\rho(1)$, being evaluated from eq. (6) at $C_{Ti}(1) = 0.8 \times 10^{-2}$, the conductivity is estimated to be about 18% IACS, which agrees well with the measured value. When the same alloy was aged in the hydrogen atmosphere,
the conductivity exceeded 18% IACS already at 1 h (data 3). This indicates that the concentration of solute Ti in the matrix decreased to less than 0.8 mol%, as a result of co-precipitation of Cu₄Ti and titanium hydride. Since the kinetics of the conductivity is similar to each other between the Cu–3 mol% Ti alloy and Cu–0.36 mol% Ti alloy (data 3 and 1 in Fig. 11), it appears that precipitation of titanium hydride begins to occur after that of Cu₄Ti is completed. It was found⁴–⁶ that Cu₄Ti particles disappear during prolonged aging and eventually only the hydride remains as the second phase. The volume fraction of the hydride of the Cu–3 mol% Ti alloy in the final stage is estimated to be 2.7%, if all of the Ti atoms are consumed to form the hydrides. The conductivity of the alloy is then expected from eqs. (6) and (7) to reach 96% IACS.

### 4.4 Precipitation strengthening by hydride particles

The yield strength, $\sigma_y$, of aged Cu–0.36 mol% Ti alloy may be expressed as follows, with solid-solution strengthening by Ti solutes in the matrix, $\Delta\sigma^{(1)}$, and precipitation strengthening by titanium hydride, $\Delta\sigma^{(2)}$,

$$\sigma_y = \sigma_{y0} + \Delta\sigma^{(1)} + \Delta\sigma^{(2)}, \quad (8)$$

where $\sigma_{y0}$ is the yield strength of pure copper, which is 25 MPa at room temperature. The rate of solid-solution strengthening by Ti, $d\sigma^{(1)}/dC^{(1)}_{Ti}$, is 32 MPa per 1 mol% Ti.⁵ One may evaluate the increase in strength by the precipitation of the hydride, $\Delta\sigma^{(3)}$, from the following equation,

$$\Delta\sigma^{(2)} = \sigma_y - \sigma_{y0} - \frac{d\sigma^{(1)}}{dC^{(1)}_{Ti}}C^{(1)}_{Ti} \quad (9)$$

The evolution of $\Delta\sigma^{(2)}$ during aging in the hydrogen atmosphere, calculated from eq. (9) using $C^{(1)}_{Ti}$ shown in Fig. 10, is shown in Fig. 12 (data 1). It reaches a maximum at 24 h, and then decreases slightly.

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**Fig. 11** Electrical conductivity of Cu–0.36 mol% Ti alloy aged at 773 K under an estimated hydrogen pressure of 0.4 MPa (No. 1), and in a vacuum (No. 2). The values of Cu–3 mol% Ti alloy aged at the same temperature in hydrogen (No. 3) and in a vacuum (No. 4) are also shown.⁹ The conductivity of solute-treated Cu–0.36 mol% Ti and Cu–3 mol% Ti (31% IACS and 5.4% IACS, respectively) are indicated by the dotted lines (a, b).

In precipitation strengthening, if the precipitate particles can be deformed plastically, dislocations in the matrix phase may proceed by cutting the particles, whereas if the particles are very hard, dislocations pass through them leaving by a dislocation loop around a particle (Orowan mechanism). Since titanium hydride is much harder than the copper solid solution,⁶,²¹,²² the strengthening by the hydride particles must be due to the Orowan mechanism, as described below.

The increase in the yield strength, $\Delta\sigma_p$, due to the Orowan mechanism is given by:²³

$$\Delta\sigma_p = \frac{0.538Gb\sqrt{f}}{d} \ln \frac{d}{2b} \quad (10)$$

Here, $G$ is the shear modulus of the matrix, $b$ is the magnitude of the Burgers vector, $f$ is the volume fraction of the particles, and $d$ is their average diameter. $\Delta\sigma^{(3)}$ was evaluated by inserting the following parameters into eq. (10): the shear modulus of pure copper for $G$ (48.3 GPa), the Burgers vector of a perfect dislocation in pure copper for $b$ (0.255 nm), the volume fraction of titanium hydride ($f^{(2)}$ in Fig. 9) for $f$, and the average diameter of the hydride particle shown in Fig. 5 for $d$. The results are plotted in Fig. 12 (data 2). As these values are close to those derived from eq. (9), the strengthening by the hydride particles is most...
probably due to the Orowan mechanism. Its contribution to the yield strength was approximately 40 MPa in the present experiment for the Cu–0.36 mol% Ti alloy aged at 773 K in the hydrogen atmosphere.

In Fig. 12 are also shown the contribution of precipitation strengthening to the yield strength of Cu–3 mol% Ti alloy aged at 773 K in a vacuum (data 4) and in the hydrogen atmosphere (data 3), which was estimated by eq. (9).\(^5\) During the aging in a vacuum (data 4), the strengthening by Cu4Ti precipitates was 370 MPa at 1 h and then it decreased because of particle coarsening. Nevertheless it is still over 280 MPa at 48 h. Upon aging in the hydrogen atmosphere, the precipitation strengthening at 1 h is virtually equal in magnitude to that rendered by the vacuum aging, because only Cu4Ti are preferentially formed at the early stage of aging.\(^5\) However, at the next stage, i.e., over 1 h, titanium hydrides begin to precipitate, and they grow at the expense of Cu4Ti particles.\(^4\)\(^6\)\(^7\)\(^8\)\(^9\)\(^5\)\(^7\)\(^8\) At this overaging stage the magnitude of precipitation strengthening, which includes contributions from Cu4Ti and the hydride particles, decreases more rapidly than in the case of the vacuum aging. This indicates that the strengthening by the hydride particles is weaker than that by Cu4Ti particles because the number density of the former particles is much smaller than that of the latter.\(^5\)\(^7\)\(^8\)\(^9\)\(^5\)\(^7\)\(^8\)\(^9\) In fact, if all of the solute Ti in the Cu–3 mol% Ti alloy are consumed to form the hydrides and the precipitation behavior (volume fraction and particle size) is same as that in the Cu–0.36 mol% Ti alloy, the increase in the strength due to the hydride particles is about 115 MPa at the maximum, as estimated from eq. (10). This is quite small in comparison with that realized by mono-precipitation of Cu4Ti precipitates in the same alloy, 370 MPa.

5. Summary

In this study, phase transformation, microstructural evolution, and electrical and mechanical properties for Cu–0.36 mol% Ti alloy aged at 773 K under a hydrogen atmosphere were investigated. On the basis of the results obtained, the precipitation behavior of titanium hydride and its influences on both electrical and mechanical properties of the specimen were quantitatively evaluated. The salient findings are summarized as follows:

1. The hydrogen content increases with aging time in the hydrogen atmosphere. The absorbed hydrogen atoms react with Ti solutes to form titanium hydride. The composition of titanium hydride is close to H/Ti = 2. The hydride particle exhibit an octahedral shape and their interfaces are parallel to [111] of the copper matrix. The crystallographic orientation relationship between the matrix and the hydride precipitate is (001)\(_m\) || (001)\(_p\) and [010]\(_m\) // [010]\(_p\), and the interfaces are semi-coherent. The size and the volume fraction of the hydride particles increase with aging time and eventually reach an equilibrium after 100 h. The number density of the hydride particles has a maximum at 24 h.

2. The electrical conductivity significantly improves during aging in the hydrogen atmosphere and eventually approaches almost 100% IACS after aging for 100 h. This is because all of Ti atoms in the alloy were consumed to form titanium hydride, and as a result the concentration of solute Ti in the matrix was reduced to almost zero.

3. The strength increases with aging in the hydrogen atmosphere, and then reaches a maximum at 24 h. The strengthening due to titanium hydride particles can be explained in terms of the Orowan mechanism. Under the aging conditions employed in this study, the maximum increase in the strength due to the hydride particles was 40 MPa.

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