Aging of Cu-3 at% Ti Alloys in Hydrogen Atmosphere: Influence of Hydrogen Pressure on Strength and Electrical Conductivity*¹

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The influence of hydrogen pressure during isothermal aging on the mechanical strength, electrical conductivity, and microstructure of Cu-3 at% Ti alloys was investigated under various hydrogen pressures from 0 to 0.8 MPa. The variation of hardness with aging time was not significantly different among all specimens aged under the hydrogen pressures. This is because the hardness is improved primarily by the precipitation strengthening of Cu₄Ti particles, which is less affected by hydrogen pressure. The electrical conductivity increased more significantly for specimens aged under higher hydrogen pressure, due to a rapid reduction in the concentration of Ti dissolved in the matrix, which is attributed to the accelerated formation of TiH₂. The conductivity at peak-hardness was improved by a factor of approximately 1.4 in the specimens aged at both 773 and 723 K under the highest hydrogen pressure, compared to that for the specimen aged in vacuum. Therefore, aging under high hydrogen pressure assisted in the significant improvement of both strength and electrical conductivity.

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1. Introduction

Among the various copper (Cu) based alloys, age-hardenable Cu-titanium (Ti) alloys are attractive as a substitute for Cu-beryllium (Be) alloys, which pose the relatively high production costs and potential health hazards of Be. The mechanical strength of Cu-Ti alloys is comparable to that of Cu-Be alloys with good stress-relaxation behavior and higher thermostability.¹⁻⁴ However, Cu-Ti alloys are inferior in electrical conductivity, due to the much larger contribution of Ti solute to the resistivity than Be.^{5,6} To extend the industrial applicability of Cu-Ti alloys for electrical parts such as lead frames and connectors, it is strongly desirable to provide Cu-Ti alloys with both high strength and high conductivity.

Semboshi and Konno recently reported that the conductivity of Cu-3 at% Ti alloy increases more significantly when aged at 773 K in a hydrogen pressure of 0.37 MPa rather than aged in vacuum.⁷ The increase was attributed to a reduction in the concentration of Ti dissolved in the matrix, as a result of the formation of the titanium hydride (TiH₂) phase. In a subsequent paper, the microstructure and mechanical properties of the alloy aged under the same conditions were reported.⁸ During the early stage of aging, fine needle-shaped precipitates of the Cu₄Ti intermetallic phase are dispersed, similar to aging in vacuum. Upon further aging, the precipitation of Cu₄Ti proceeds and TiH₂ particles are spontaneously formed by the combination of diffused hydrogen with Ti in the matrix and in the Cu₄Ti precipitates. The hardness was increased with aging time and exhibited a peak at 1 to 3 h, which was essentially similar to the case of aging in vacuum. Recently, it was found that aging at a low

temperature was useful for improving both the strength and conductivity.⁹ For example, aging at 673 K under the hydrogen pressure of 0.08 MPa resulted in an increase of the conductivity at peak-hardness that was more than twice as high as that of the same alloy aged in vacuum, although a long time (ca. 1 month) was required.

In order to prepare Cu-Ti alloys with high strength and high conductivity by aging in hydrogen atmosphere, it is important to control the microstructural evolution, such as precipitations of Cu₄Ti and TiH₂ phases. It is therefore required to understand the influence of hydrogen pressure during aging, in addition to aging temperature, because it must influence directly on the formation of the TiH₂. In the present work, Cu-3 at% Ti alloys was isothermally aged under hydrogen pressures between 0 and 0.8 MPa to clarify the influence on the resulting hardness and conductivity. The microstructure was also examined using transmission electron microscopy (TEM) and X-ray diffraction (XRD) to confirm the relationship between their microstructure and properties.

2. Experimental Procedure

A button ingot with a nominal composition of Cu-3 at% Ti was prepared by arc-melting 99.99% pure copper and 99.99% pure titanium as raw materials in argon atmosphere. The ingot was annealed at 1073 K for 24 h in vacuum for homogenization. The ingots were cold-rolled and subsequently cut into plates measuring 50 × 5 × 0.8 mm³. The specimens were solution-treated at 1073 K for 12 h in vacuum and quenched in water. In order to remove the surface oxide layer, the specimens were ground with 2000 grade SiC paper, and then rinsed in acetone. The plates were aged at 773 and 723 K in vacuum or under hydrogen pressures of 0.08 to 0.8 MPa, using 99.99999% pure hydrogen gas.

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The Vickers hardness was examined with an applied load of 500 g and a holding time of 10 s. The hardness number was determined by averaging the results of more than ten tests, excluding the maximum and minimum values. The electrical conductivity of the aged specimens was measured at room temperature using the standard DC four-probe technique. The hydrogen content of the specimens was analysed by the fusion thermal conductivity method with argon as carrier gas,¹⁰⁾ using a hydrogen analyzer HORIBA EMGA-621W. The microstructure of specimens aged at 773 K under hydrogen atmospheres of 0.2 and 0.5 MPa was examined by TEM. Thin-foil samples for TEM observations were first ground to less than 80 μm in thickness and then electro-polished in a solution of 5.0 vol% nitric acid in methanol at 243 K with a DC voltage of less than 10 V, followed by low-angle ion milling with an argon ion beam accelerated at 3 kV. XRD patterns were obtained using Cu K α radiation. The lattice parameters were determined by extrapolating the values measured from the XRD profiles to $\theta = 90$ degree as a function of $\cos^2 \theta$. The content of Ti dissolved in the matrix phase was estimated from the lattice parameter using Vegard's law.^{7,11)}

3. Results and Discussion

3.1 Hardness and electrical conductivity

Figures 1(a) and (b) show the variations of hardness and electrical conductivity for the Cu-3 at% Ti alloys, respectively, during aging at 773 K in vacuum and under hydrogen pressures of 0.08 to 0.5 MPa. The results for specimens aged under the hydrogen pressure of 0.08 and 0.37 MPa were taken from previous studies.⁷⁻⁹⁾ For all these hydrogen pressures, the hardness increased with aging time and then reached the maximum after 1 to 3 h, although the hardness appeared to be only slightly lower by aging under higher hydrogen pressure (see Fig. 1(a)). Figure 1(b) shows that the conductivity increased more rapidly by aging under higher hydrogen pressure. The conductivity of the specimen aged under the hydrogen pressure of 0.5 MPa reached approximately 70% IACS (%IACS: percentage based on the electrical conductivity of the International Annealed Copper Standard at 298 K, $5.80 \times 10^7 \Omega^{-1}\text{m}^{-1}$) after 48 h, which was approximately four times as high as the maximum conductivity of the specimen aged in vacuum.

Figures 2(a) and (b) show the variations of the hardness and electrical conductivity, respectively, during aging at 723 K in vacuum and under hydrogen pressures of 0.08 to 0.8 MPa. The values of the specimen aged under the hydrogen pressure of 0.08 MPa were taken from a previous study.⁸⁾ The variation of hardness and conductivity with aging time was substantially similar to that for aging at 773 K; the aging time to reach the peak-hardness was almost the same, approximately 18 h, for all the hydrogen pressures, whereas the hardness was slightly lower and the conductivity was higher when aged in higher hydrogen pressure.

Figures 3(a) and (b) show the variations of peak-hardness and conductivity at peak-hardness, respectively, with respect to the hydrogen pressure for aging at 773 and 723 K. It should be noted that the values used were those for specimens aged for 3 h at 773 K and for 18 h at 723 K. For aging both at 773

Fig. 1 Variations of (a) Vickers hardness and (b) electrical conductivity for Cu-3 at% Ti alloys aged at 773 K in vacuum, and under hydrogen pressures of 0.08,⁹⁾ 0.2, 0.3, 0.37^{7,8)} and 0.5 MPa.

and 723 K, the peak-hardness decreased gradually with increased hydrogen pressure, as shown in Fig. 3(a). However, the ratio of decrease was only within 6%, based on the value of aging in vacuum. On the other hand, the conductivity at peak-hardness increased significantly with increased the hydrogen pressure, as shown in Fig. 3(b), and the ratio of increase was approximately 38% for the specimen aged at 773 K in the hydrogen pressure of 0.5 MPa and approximately 43% for that aged at 723 K in 0.8 MPa. Therefore, it can be concluded that aging under high hydrogen pressure is available for improvement of both the peak-hardness and the conductivity at peak-hardness.

From a practical viewpoint, the peak-hardness and the conductivity at peak-hardness are the most important properties, because a high conductivity is required for age-hardenable Cu-Ti alloys without degradation of the mechanical properties. It has been previously reported that aging at low temperature, T , was effective to improve both the strength and conductivity of Cu-Ti alloys.⁸⁾ However, it takes a much longer time to achieve such by aging at a lower temperature, because the aging time to reach peak-hardness is proportional

Fig. 2 Variations of (a) Vickers hardness and (b) electrical conductivity for Cu-3 at% Ti alloys aged at 723 K in vacuum, and under hydrogen pressures of 0.08,⁹⁾ 0.2, 0.5 and 0.8 MPa.

to $\exp(T^{-1})$. In this study, we have demonstrated that aging in high hydrogen pressure can be used for improvement of the conductivity at peak-hardness of Cu-Ti alloys, and that the aging time to reach the peak-hardness was not significantly altered with the hydrogen pressure. Therefore, an increase of the hydrogen pressure during aging is available to provide a reasonably good combination of both strength and conductivity, even if the aging temperature is not low.

3.2 Microstructural evolution

Figure 4 shows the hydrogen contents of specimens aged at 773 K in vacuum and under the hydrogen pressures of 0.2, 0.37 and 0.5 MPa for various aging times. The hydrogen contents of the specimen aged under a hydrogen pressure of 0.37 MPa were taken from a previous study.⁷⁾ The hydrogen contents of the specimens quenched and aged in vacuum were less than 0.01%, whereas that of the specimen aged under a the hydrogen pressure of 0.2 MPa increased with aging time and reach approximately 4.7 at% at 96 h. The hydrogen content increased more rapidly for the specimens aged under higher hydrogen pressure.

Fig. 3 Variations of (a) peak-hardness and (b) electrical conductivity at peak-hardness for Cu-3 at% Ti alloys aged at 773 and 723 K under hydrogen pressure. The aging time to peak-hardness was 3 h at 773 K and 18 h at 723 K.

Fig. 4 Variation of hydrogen content in Cu-3 at% Ti alloys aged at 773 K in vacuum, and under hydrogen pressures of 0.2, 0.37⁸⁾ and 0.5 MPa.

The microstructural evolution of a specimen aged at 773 K in a hydrogen atmosphere at 0.37 MPa has been investigated;⁸⁾ finely dispersed precipitates of Cu_4Ti were formed during the early aging stage, and subsequently particles of titanium hydride, TiH_2 , were also formed by reaction of dissolved hydrogen atoms with Ti atoms in the matrix or in Cu_4Ti precipitates. The precipitation behavior of Cu_4Ti was similar to the specimens aged at the same temperature of 773 K under the hydrogen pressures of 0.2 to 0.5 MPa, whereas the formation of TiH_2 was promoted by increasing the hydrogen pressure for aging, as described below.

Fig. 5 Bright field transmission electron microscope (BF TEM) images and selected area diffraction (SAD) patterns viewed along the [001] zone axis for Cu-3 at% Ti alloys aged at 773 K for 3, 12, and 48 h under hydrogen pressures of 0.2 and 0.5 MPa. The weak spots marked by dotted circles in (a) are those in the 001 diffraction pattern of Cu_4Ti . The weak spots shown in (b) are from TiH_2 , which was taken from the rhombic contrast, and representative examples are indicated by solid circles in the BF TEM image.

Figure 5 shows bright field (BF) TEM images and selected area diffraction (SAD) patterns of specimens aged at 773 K for 3, 12, and 48 h under hydrogen pressures of 0.2 and 0.5 MPa. The BF TEM image of the specimen aged for 3 h under the hydrogen pressure of 0.2 MPa is dominated by characteristic needle-shaped contrasts aligned in the $\langle 001 \rangle_{\text{Cu}}$ directions. The contrasts are due to coherency misfit strain arising from Cu_4Ti precipitates (space group $I4/m$ with lattice parameters $a = 0.584$ nm, $c = 0.362$ nm^{1,4,12}), which was confirmed by the corresponding SAD pattern. On aging at 12 h, the BF TEM image shows coarsened needle-shaped Cu_4Ti precipitates of approximately 100 nm in length, and rhombic contrasts of approximately 50 nm in size, as indicated by the solid circle. The latter is attributed to TiH_2 ($Fm\bar{3}m$ with $a = 0.444$ nm^{13,14}) as identified by the SAD pattern. On aging at 48 h, some needle-like Cu_4Ti precipitates of more than 100 nm in length were present, but rhombic TiH_2 particles of approximately 50 nm were predominant in the specimen. On the other hand, for the specimen aged under the hydrogen pressure of 0.5 MPa, rhombic TiH_2 particles were already formed together with needle-shaped Cu_4Ti after 3 h. On further aging after 12 h, only rhombic contrasts due to TiH_2 were observed in the Cu matrix phase, which suggests that almost all of the Cu_4Ti precipitates were decomposed to TiH_2 and Cu during the earlier period of aging than in the case of hydrogen pressure of 0.2 MPa.

Fig. 6 Lattice parameters and Ti solute content in the Cu-3 at% Ti alloy matrix aged at 773 K in vacuum and under hydrogen pressures of 0.2 and 0.5 MPa. The lattice parameters of pure copper and as-quenched Cu-3 at% Ti specimen were 0.3615 and 0.3628 nm, respectively.

Figure 6 shows the lattice parameters and Ti content in the matrix estimated from the lattice parameters of specimens aged at 773 K in vacuum and under hydrogen pressures of 0.2 and 0.5 MPa for various aging times. The lattice parameters

of the specimens decreased with aging time, with an equivalent decrease in the content of Ti in the matrix. After 24 h aging in vacuum, the Ti content in the matrix remained at approximately 0.8 at%, which agrees well with the solid solubility limit at 773 K evident from the Cu-Ti binary phase diagram.¹⁵⁾ When aged in a hydrogen atmosphere, the Ti content in the matrix decreased significantly and rapidly under higher hydrogen pressures, due to the accelerated formation of TiH₂.

3.3 Effects of hydrogen pressure on aging

The effect of hydrogen pressure during aging on the hardness and conductivity of the specimens can be explained by the microstructural evolution; the hardness of the specimen should be modelled by the superposition of solid solution hardening and precipitation hardening of Cu₄Ti and TiH₂ particles. During the early stage of aging, hardening of the specimen is primarily due to precipitation of Cu₄Ti, which progresses independently of the hydrogen pressure used. Therefore, the aging time to attain maximum hardness is less affected by the hydrogen pressure. On the other hand, the formation of TiH₂ particles with further aging is accelerated by an increase of hydrogen pressure as indicated in Fig. 5, which leads to a rapid reduction of the Ti content in the matrix and the rapid decomposition of pre-formed Cu₄Ti particles. Therefore, hardening by solid solution and by precipitation of Cu₄Ti becomes weakened in a specimen aged under a higher hydrogen pressure, although hardening due to the precipitation of TiH₂ emerges. The total amount of hardening should be eventually decreased by aging under a high hydrogen pressure, which would result in a slight decrease of hardness, as shown in Fig. 3(b). In addition, the significant reduction in the Ti concentration in the matrix by precipitation of TiH₂ directly contributes to the marked increase in the conductivity of the specimen, which obeys Nordheim's rule;^{11,16)} therefore, the conductivity increases more significantly with higher hydrogen pressure.

4. Conclusion

The effect of hydrogen pressure (0 to 0.8 MPa) during isothermal aging on the hardness and electrical conductivity of Cu-3 at% Ti alloys was investigated, together with the microstructural evolution. The salient results obtained are summarized as follows.

- (1) The aging time to attain a maximum hardness was almost the same for all of the specimens aged at the same temperature, regardless of the hydrogen pressure. The hardness decreased slightly, whereas the conductivity increased significantly with increasing hydrogen pressure. As a result, aging in a high hydrogen pressure

led to a significant improvement of both the mechanical and electrical properties.

- (2) During the early stage of aging, fine needle-shaped Cu₄Ti precipitates were dispersed in the matrix, which were little affected by the hydrogen pressure. As the aging progressed, Cu₄Ti was precipitated and TiH₂ particles were spontaneously formed by the combination of diffused hydrogen with Ti in the matrix and in Cu₄Ti precipitates. The formation of TiH₂ particles was promoted by aging under high hydrogen pressure and resulted in a rapid reduction of Ti content in the matrix.

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