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Microstructural evolution of Cu-1 at% Ti alloy aged in a hydrogen atmosphere and its relation with the electrical conductivity

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ABSTRACT

Copper alloys with titanium additions between 1 and 6 at% Ti emerge currently as attractive conductive materials for electrical and electronic commercial products, since they exhibit superior mechanical and electrical properties. However, their electrical conductivity is reduced owing to the residual amount of Ti solutes in the Cu solid solution (Cu_{ss}) phase. Since Cu shows only poor reactivity with hydrogen (H), while Ti exhibits high affinity to it, we were inspired by the idea that hydrogenation of Cu–Ti alloys would influence their microstructure, resulting in a significant change of their properties. In this contribution, the influence of aging under a deuterium (D_2) atmosphere of Cu-1 at% Ti alloys on their microstructure is investigated to explore the effects on the electrical conductivity. The specimens were investigated by means of transmission electron microscopy (TEM), field ion microscopy (FIM), computer-aided field ion image tomography (cFIIT), and atom probe tomography (APT).

At an early aging stage at 623 K in a D_2 atmosphere of 0.08 MPa, ellipsoidal α-Cu_4Ti precipitates are formed in the alloy, and during subsequent aging, δ-TiD_2 is competitively nucleated instead of growth of α-Cu_4Ti particles. The co-precipitation of α-Cu_4Ti and δ-TiD_2 efficiently reduces the Ti concentration of Cu_{ss} matrix, particularly in the later aging stages in comparison to the aging in vacuum conditions. The electrical conductivity of the alloy aged in the D_2 atmosphere increases steeply up to 48% International Annealed Copper Standard (IACS) after 1030 h, while it saturates to approximately 20% IACS in the alloy aged in vacuum. The outstanding increase of electrical conductivity during aging in D_2 atmosphere can be basically explained by the reduction of Ti solute concentration in Cu_{ss} matrix.

1. Introduction

Copper and copper-based alloys are widely used for numerous applications that require high mechanical properties, resistance to corrosion, and electrical conductivity. Among the alloys having a good combination of strength and electrical conductivity, age-hardenable Cu–Be-based alloys have been commercially applied. Unfortunately, these materials have the restriction of high cost of production and in particular, potential health hazard associated with Be. As a substitute material for the Cu–Be alloys, the age-hardenable Cu-Ti alloys containing approximately 1–6 at% Ti are attractive because the mechanical properties such as thermal strength and stiffness are even superior to those of Cu–Be alloys [1–4]. However, electrical conductivity of the Cu–Ti alloys is inadequate owing to the high concentration of Ti solutes in the Cu solid solution (Cu_{ss}) phase [5,6]. Therefore, it appears as a crucial challenge to find a way to enhance the electrical conductivity of Cu–Ti alloys in order to extend their applicability among the electronic engineering fields.

Recently, Semboshi and Konno [7] reported that the electrical conductivity at room temperature of the Cu-3 at% Ti alloy aged at 773 K for 48 h in hydrogen atmosphere reached a value more than three times as high as that aged in vacuum conditions; the high conductivity was attributed to reduction of the concentration of Ti solutes in the Cu_{ss} matrix, which was indicated by X-ray diffraction as variation of the lattice parameter. In addition, formation of α-Cu_4Ti and titanium hydride (δ-TiH_2) precipitates during the aging was indicated by electron diffraction. In this work, we investigate in detail the structural evolution of Cu-1 at% Ti alloys aged in deuterium (D_2) atmosphere by means of transmission electron microscopy (TEM), field ion microscopy (FIM), and atom probe tomography (APT). The electrical conductivity has also been examined as a function of aging time to discuss the relationship between microstructural evolution and electrical conductivity of the alloy.

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Since, it has been often reported that during the APT analysis, hydrogen and hydrocarbons within the residual gas of the vacuum system lead to a considerable background signal for hydrogen, deuterium isotope was used in this study to avoid any confusion.

2. Experimental procedure

A button ingot with the nominal composition of Cu-1 at% Ti was prepared by arc melting in argon atmosphere, using 99.99% copper and 99.99% titanium as start materials. The ingot was homogenized at 1073 K for 24 h in vacuum, followed by cold drawing and cutting into wires measuring approximately 70 mm in length and 0.25 mm in diameter. The wires were then again solution treated at 1073 K for 3 h and quenched in water. Immediately after removing the oxide layer on the wires by grinding the surface with 2000 grade of SiC paper, they were aged at 623 K for various durations up to 1030 h in D_2 atmosphere under the pressure of 0.08 MPa or in vacuum ($<2\times10^{-2}$ Pa) for comparison.

The microstructure of the alloy aged in the D_2 atmosphere was investigated by TEM using JEOL JIM-2000FX, operating at 200 kV. The TEM specimens were prepared by utilizing the lift-out method in a focused ion beam (FIB) FEI Quanta 3D. The specimens for FIM and APT measurement were prepared using standard electrochemical polishing utilizing as an electrolyte a mixture of sodium chromate and acetic acid (1:10) at 293 K, applying a voltage of 12–14 V at room temperature. FIM images were recorded using Ne as imaging gas between 30 and 60 K. TAP analyses were performed with the following parameters: base voltage of 6.0–14.95 kV with 22% pulse to base fraction, 2000 Hz repetition rate, and 30 K acquisition temperature. The electrical resistivity of the alloys was measured at room temperature using a standard DC four-probe technique by a micro-ohm meter Agilent, which was converted to electrical conductivity.

3. Results and discussion

3.1. Structural evolution

Fig. 1(a) shows a bright field (BF) image of the Cu-1 at% Ti alloy aged at 623 K for 430 h in the D_2 atmosphere and the inset represents a selected area diffraction (SAD) pattern, viewed close to $[0\,0\,1]_{Cu}$ zone axis. The SAD pattern agrees with the superposition of fundamental spots arising from Cu_{ss} matrix having the fcc structure (the lattice parameter $a=0.361$ nm), and weak superlattice spots at the position of 1/5 $(420)_{Cu}$ and equivalent ones, as marked by solid circles. The latter are assigned to α-Cu_4Ti with a body-centered tetragonal structure ($a=0.584$ nm, $c=0.362$ nm) [3,4]. The BF image is dominated by characteristic strain contrasts caused by the precipitation of α-Cu_4Ti phase, which is coherent with the matrix [8,9], having an average size of approximately 5 nm in c-direction of the ellipsoidal.

Fig. 1(b) is a BF image of the alloy aged for 1030 h in the D_2 atmosphere, and an inset SAD pattern viewed again close to $[0\,0\,1]_{Cu}$ zone axis. In the SAD pattern of this figure, weak spots, as marked by dotted circles, are assigned to the δ-TiD_2 phase having the fcc structure of $a=0.445$ nm [10], which is consistent with the previous work [7]. No spots corresponding to α-Cu_4Ti phase were detected in the SAD pattern. The BF image of Fig. 1(b) shows less strain contrasts caused by α-Cu_4Ti precipitates than that of Fig. 1(a), while we could not identify clearly other contrasts arising from δ-TiD_2 phase. From this TEM observation, and the results obtained on the higher super-saturation in the previous results [7], it is proposed that δ-TiD_2 is competitively formed instead of α-Cu_4Ti phase in the latter aging in the D_2 atmosphere.

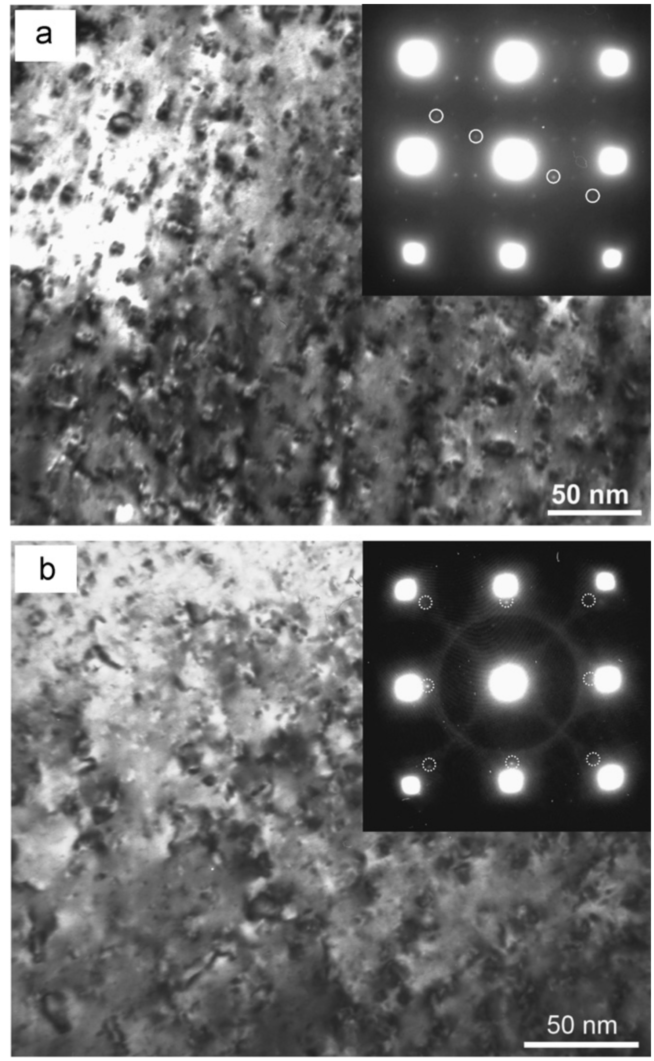

Fig. 1. BF images and SAD patterns of the Cu-1 at% Ti alloy aged at 623 K for 430 h (a), and for 1030 h (b) in a D_2 atmosphere at the pressure of 0.08 MPa. The BF image of (a) shows strain contrasts arising from precipitates approximately 5 nm in length, and the inset SAD pattern shows the presence of superlattice spots at 1/5 (420) and its equivalent positions, as indicated by solid circles, suggesting the formation of α-Cu_4Ti phase. The SAD pattern in (b) shows the presence of weak spots as indicated by dotted circles suggesting the formation of δ-TiD_2 phase.

Fig. 2 shows indexed FIM images of Cu-1 at% Ti alloys that were quenched (a), aged for 90 h (b), and 430 h (c) at 623 K in the D_2 atmosphere, and aged for 430 h in vacuum (d). The FIM image of the quenched alloy (Fig. 2a) shows a typical pattern of an fcc structure, suggesting that the alloy consists of homogeneous Cu_{ss} phase. In the alloy aged in the D_2 atmosphere for 90 h (cf. Fig. 2b), only a pattern assigned to the Cu_{ss} matrix was detected. In the alloy aged for 430 h (c), we can find both the pattern relating to the Cu_{ss} matrix and also some bright contrasts with the size of several nano-meters as indicated by the arrows. The latter surely corresponds to α-Cu_4Ti precipitates, because they have the similar size as the precipitates in the TEM image (Fig. 1(a)). In the alloy aged for 430 h in vacuum (Fig. 2d) we can also see bright contrasts probably corresponding to α-Cu_4Ti precipitates, as marked by the arrows.

The bright contrasts from the α-Cu_4Ti precipitates in Figs. 2(c) and (d) were relatively clear in some region. Therefore, three-dimensional (3D) computer-aided field ion image tomography