

# An Investigation of Mechanical Degradation of Pure Copper by Hydrogen

Salman A. AL Duheisat

Al-Balqa Applied University, Faculty of Engineering Technology  
P. O .Box 1500 Amman 11134 Jordan,

Copyright © 2014 Salman A. AL Duheisat. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

## Abstract

The effect of hydrogen on the mechanical properties of pure copper was investigated after experiments conducted on specimens that hydrogen charged under different cathodic charging conditions. Cathodic hydrogen charging was found to reduce the ductility and ultimate tensile strength of the copper. These parameters are decreased with increasing the current density and charging time. The fracture surfaces of the charged tensile specimens consisted of mixed fracture mode, brittle fracture was found in the outer periphery of the cross sectional areas while ductile fracture was observed in the center of the fracture surfaces of the hydrogen charged tensile copper specimens. Microhardness measurements revealed that the introduction of hydrogen caused hardening on the surface of copper. The severity of the hardened region increased with either cathodic current density or charging time. Further charging increased the depth of the hardened region of copper. Ageing after charging can result in either complete or partial recovery of hardness, depending on the charging conditions.

**Keywords:** Cathodic Hydrogen Charging, Copper, Microhardness, Tensile Properties

## INTRODUCTION

The deleterious effects of hydrogen on the strength and ductility of metals and alloys have been studied by a numerous investigators. Watson et al. [1] studied the effect of

cathodic hydrogen charging on the mechanical properties of pure aluminum and it was found that the cathodic charging reduced the ductility and increased the yield and tensile stresses of pure aluminum.

Kimura and Birnbaum [2] found that embrittlement of high purity nickel by solute hydrogen is accompanied by a change in fracture mode from ductile rupture to an intergranular mode. It was concluded that the kinetics of intergranular embrittlement of nickel from an external hydrogen source are controlled by grain boundary diffusion of hydrogen, and the fracture occurs when a critical concentration of hydrogen attained at the grain boundaries.

Panagopoulos and Papapanayiotou [3] studied the effect of cathodic hydrogen charging on the mechanical behavior of Al-4Zn-1Mg and noted that the ultimate tensile stress of the charged aluminum alloy was to be a non-linear function of the charging current density. The last investigators observed that the cathodically charged aluminum alloy exhibited brittle transgranular fracture at the surface layer, whereas ductile intergranular fracture was observed at the deeper layers. Hydrogen embrittlement was observed in high purity iron by Akihiko Kimura and H. Kimura [4], These investigators found that the embrittlement is observed regardless of hydrogen hardening or softening.

The effect of hydrogen on hardness of the metallic materials has been also reported by several investigators. A. Lost and J.B. Vogt [5] studied the hydrogen-enriched surface of an austenitic stainless steel with the microhardness tests. They found that cathodic hydrogen charging changes the Vickers hardness number (VHN) values of the material. The variations of (VHN) were related to the hydrogen content in the  $\gamma$ -lattice. It was concluded that the increase in VHN by cathodic hydrogen charging of the material is associated with an increase in the compressive stresses resulting from the diffusion of hydrogen in the  $\gamma$ - lattice.

It was found that cathodic hydrogen charging of Al-4Zn-1Mg alloy produced major surface hardening. They observed that the microhardness increased with both the charging current density and charging time. Their observations have been explained in terms of the dislocation pinning mechanism. They found that the microhardness of Al-4Zn-1Mg decreased during natural ageing. It was concluded that the surface layer did not recover to its prior-to-charging hardness with the time passed after charging [3].

The objective of this work was to determine the effect of cathodic hydrogen charging on mechanical properties of copper. The effects have been further examined with optical and scanning electron observations of the near-fracture and fracture surfaces of the copper tensile specimens. Also a considerable amount of work has been made to determine the penetration depth of cathodically charged hydrogen into the copper specimens using microhardness measurements conducting on the charged, near-charged and interior surfaces.

## EXPERIMENTAL PROCEDURE

The material used in this investigation was pure copper sheet of 1mm in thickness. Tensile experiments were conducted on specimens of full-size tubular sections with a

25cm gauge length according to ASTM E8 methods for tension testing. In order to permit the testing machine jaws to grip these specimens properly, metal plugs were inserted into the end of these. The central portion of each specimen was electropolished.

For the microhardness measurements, a number of specimens were cut from this tube with 10mm width.

All the specimens were annealed for one hour at 300°C, and then slowly cooled to room temperature in a furnace to relieve residual stresses induced from machining.

Prior to cathodic charging, any thick or substantial oxide or hydroxide layer present on the surface, which might act as a barrier to hydrogen uptake, was removed by slightly polishing the samples on 600-grit paper, then electrolytically polished and finally pickled in a solution of 5 parts nitric acid, 5 parts orthophosphoric and 1 part acetic acid.

Electrolytic polishing was done at 1.5V using a stainless steel cathode in a solution of 40 vol.% orthophosphoric and 60vol.% water at room temperature. These steps are very important in order to promote the hydrogen entrance and for obtaining reliable measurements.

The cathodic hydrogen charging technique developed in the laboratory consists of graphite anode. The graphite anodes have rather high mechanical strength and electrical conductivity, and they can be readily machined. The specimen was made cathode in the electrolytic cell. The electrolytic solution contains 75% (volume) methanol, 22.4% (volume) distilled water, 2.6% (volume) sulphuric acid and 10mg per liter arsenic trioxide to inhibit hydrogen recombination at the surface. Constant current densities of between 5 and 85mA.cm<sup>-2</sup> were applied to the specimens. The hydrogen charging time varied from 5 hour up to 72hours. The charging of hydrogen into these specimens was provided from the interior surface of the tube specimens. The experiments were performed at room temperature.

The tensile tests were carried out at a strain rate of  $2.4 \times 10^{-4} \text{ S}^{-1}$ , at room temperature, in air. The load-elongation curves (stress-strain curves) were recorded on a strip chart, from which strength and ductility data were calculated. Ductilities of specimens were evaluated by the total elongation, i.e. the total strain to fracture.

The fractured surfaces of the charged specimens were examined using a scanning electron microscope. The surfaces of a longitudinal section of the fractured specimens were examined using an optical microscopy.

The microhardness was measured immediately after cathodic hydrogen charging and after various time intervals. Microhardness measurements were made across the thickness (perpendicular to tubing axis). Indentation measurements were carried out with a Vickers indenter a 25gr load for 20 seconds. Each measurement was the average of three indentations.

## **RESULTS AND DISCUSSION**

### *-Strength and ductility degradation*

Engineering stress-strain curves of uncharged and hydrogen-charged copper specimens at the two charging current densities are compared in figure 1. The

mechanical properties calculated from these curves for uncharged and hydrogen-charged copper specimens are summarized in table 2. The results indicate that cathodic hydrogen charging decreases both ultimate tensile strength (UTS) and ductility of the copper specimens. The ultimate tensile strength was decreased by hydrogen from 368 MPa to 357 MPa for the specimen cathodically charged at  $15\text{mA}\cdot\text{cm}^{-2}$  and to 321 MPa for other specimen charged at  $65\text{mA}\cdot\text{cm}^{-2}$ . The loss of the strength observed is probably due to cracking caused by hydrogen on the surface of the copper specimens. Grain boundaries, subgrain boundaries and dislocation pile-ups could act as crack-initiating sites (3).

The elongation at fracture was decreased by hydrogen from 67% to 61% for cathodically charged specimen at  $15\text{mA}\cdot\text{cm}^{-2}$  and to 44% for charged specimen at  $65\text{mA}\cdot\text{cm}^{-2}$ . The reduction in ductility may be attributed to the incorporation of hydrogen gas bubbles during cathodic charging (3).

#### *-Characteristics of fracture surfaces*

The characteristic of the fracture surfaces of copper tensile specimens also varied with the applied cathodic current density. Figure 2 shows the fracture surface of uncharged copper specimen tested in tension. The fractograph shows a dimpled surface typical of microvoid coalescence. Figures 3 and 4 show the fracture surfaces of copper specimens cathodically hydrogen charged at  $15\text{mA}\cdot\text{cm}^{-2}$  and  $65\text{mA}\cdot\text{cm}^{-2}$  current densities and then tested in tension respectively. As can be seen from these figures, the outer areas the fracture surfaces of cathodically charged copper exhibit brittle fracture, while the inside areas are still ductile. The fracture surface of the specimen cathodically charged at  $65\text{mA}\cdot\text{cm}^{-2}$  current density exhibited larger brittle area than that of the specimen cathodically charged at  $15\text{mA}\cdot\text{cm}^{-2}$  current density. It is believed that cathodic hydrogen charging at a  $65\text{mA}\cdot\text{cm}^{-2}$  current density provides a higher hydrogen fugacity than the charging condition of  $15\text{mA}\cdot\text{cm}^{-2}$  current density, which resulted in larger brittle area.

The cross-sectional views of the specimens charged at the current densities of 5 and  $65\text{mA}\cdot\text{cm}^{-2}$  and fractured in tension are shown in figures 5(a) and (b) respectively. Several microcracks can be seen in both specimens. At low current density (i.e.  $15\text{mA}\cdot\text{cm}^{-2}$ ), the microcracks are formed only near the external surface of the specimen as shown in figure 5(a), however, at higher current density (i.e.  $65\text{mA}\cdot\text{cm}^{-2}$ ) the microcracks are formed throughout the entire cross section and can be seen even at the center of the specimen 5(b).

#### *- Surface Microhardness Measurements*

Microhardness measurements revealed that cathodic hydrogen charging caused hardening on the surface of copper specimens. Microhardness measurements made on the surface intermittently during cathodic charging revealed that the hardness increases with either current density or charging time. The effect of charged hydrogen can be explained in terms of the dislocation pinning mechanism. Surface hardening must be attributed to solute hydrogen and dislocation pinning at the surface region. Solute hydrogen atoms act as dislocation pinning sites contributing to the work hardening of the alloy (3). It is believed that higher charging current density leads to higher hydrogen fugacity while higher charging time leads to higher solute hydrogen concentration, both

leading to more effective pinning of the dislocations and, therefore, decreased dislocation mobility which resulted in the hardening of the material (3).

The effect of the cathodic current density on surface microhardness of copper is shown in figure 6. It is clear that the hardness increased rapidly after charging at approximately  $15\text{mA}\cdot\text{cm}^{-2}$ . Cathodic charging at lower cathodic current densities showed no change in the hardness as shown in this figure. Thus, the charging at lower cathodic current densities may be not enough to provide a sufficient concentration to saturate the surface region of the specimen and hence to affect the hardness. The same figure shows the percentage increase of microhardness as a function of cathodic current density for a constant charging time (bold curve with respect to the secondary x-axis) which was calculated referring to the uncharged specimen. As can be seen from this figure the maximum percentage increase of microhardness  $\Delta(\text{MH})_{I_{\text{CD}}}$  is 64 %.

The effect of the charging time on surface microhardness of copper is shown in figure 7. It is clear that the hardness increased rapidly after approximately 10 hours charging. Cathodic charging for shorter time showed also no change in the hardness as shown in this figure. Thus the short-time charging may also be not enough to provide a sufficient concentration to saturate the surface region of the specimen and hence to affect the hardness. The percentage increase of microhardness as a function of hydrogen charging time (the current density was maintained at a constant value) is also shown in this figure. As can be seen from this figure, the maximum percentage increase of microhardness  $\Delta(\text{MH})_{t_{\text{CH}}}$  is 80%. However, in contrast with the  $\Delta(\text{MH})_{I_{\text{CD}}}$ , the  $\Delta(\text{MH})_{t_{\text{CH}}}$  is seen to be higher. This revealed that cathodic hydrogen charging for longer times produced a more severely hardened surface region than that of charging condition of higher current densities when the charging time has maintained at a constant value.

This observation may due to the different saturation levels of the surface region achieved by the two previous cathodic charging conditions, since the surface region is more quickly saturated during the cathodic charging at higher current densities than those of long-time of charging. Furthermore, the results confirmed that the long-time charging causes to hydrogen to diffuse into the specimen, while the diffusion of hydrogen during the charging at higher current densities might limit to the surface region.

#### *-Depth of Hardening*

Additional microhardness measurements were made across the thickness (perpendicular to tubing axis) and along the periphery of charged specimen to examine the depth and the hardness of different areas through the charged surface layer. The results of the microhardness measurements across the thickness (perpendicular to tubing axis) of the charged specimen revealed a severely hardened region near the charged surface and a less severely hardened region in the interior as compared to the uncharged specimen. The near-charged and the interior surfaces are indicated by A, B and C respectively. The severity of microhardness on these areas as a function of current density and charging time are shown in figures 8 and 9 respectively. It is clearly shown that the specimens charged for longer time exhibited higher hardness on the mentioned areas.

It was found from the test results that the depth of the hardened region increased with either the cathodic current density or charging time. The effect of the cathodic current density on the depth of hardening across the thickness (perpendicular to tubing axis) of the copper specimens is shown in figure 10. Based on the results shown in this figure, a charging at cathodic current density of  $15\text{mA}\cdot\text{cm}^{-2}$  showed no comparable hardening near the charged surface of copper specimen, only the charged surface layer was hardened as observed above. This indicated that the near-charged surface had not achieved saturation to affect the hardness during this cathodic charging condition. However a cathodic charging condition of  $25\text{mA}\cdot\text{cm}^{-2}$  current density region showed a severely hardened region near the charged surface and a less severely hardened region in the interior as revealed by the microhardness measurements, which were conducted on these regions. This result showed that the near-charged surface was saturated during the cathodic charging condition of  $25\text{mA}\cdot\text{cm}^{-2}$  current density. The further increase in the current density resulted in an increase the depth of the hardened surface region as shown in figure 10.

The effect of the charging time on the depth of hardening across the specimen thickness was also examined for copper specimens, which were cathodically hydrogen charged for different times (figure 10 bold curve). Microhardness measurements, which were conducted on the near-charged surface layer of the copper specimen charged for 12 hours (the current density was maintained at a constant value) revealed a slight hardening in this region. However, no comparable hardening of the interior region was observed. Consequently, cathodic charging for 24 hours showed a severely hardened region near the charged surface and a less severely hardened region in the interior. These results confirmed that the near-charged surface was saturated while the interior had achieved less saturation after 24 hours charging. However, charging beyond 40 hours showed that both the near-charged and the interior surfaces had achieved saturation as revealed by the microhardness measurements conducted on these surfaces. The further charging appears to increase the depth of the hardened surface region as shown in figure 10 (bold curve).

It was noted that the further cathodic charging and the further increase in the current density appear to increase the microhardness of the external and the interior surfaces of copper specimens. This phenomenon existed because of the large concentration generated at these surfaces which may cause a decrease in the dislocation mobility. However hydrogen was observed to increase the mobility of the dislocation in aluminum alloy [1]. When the introduction of hydrogen was stopped, the dislocation behavior reverted to that prior to the introduction of hydrogen. It was observed that hydrogen causes softening in nickel (6,7) and iron (8,9) due to a reduction of the resistance to dislocation motion and/or easier cross-slip resulting from a higher vacancy concentration in the presence of hydrogen. Hydrogen-induced softening is also observed at temperature between 190 and 300 K and is caused by the enhanced mobility of screw dislocations due to hydrogen (10). Below 190 K and typically around 170 K, hydrogen causes softening if the concentration of hydrogen is small, while a sufficiently high

hydrogen concentration causes hardening. The hardening is considered to be due to the interaction of hydrogen clusters with the edge component of dislocations (11).

It is concluded (4) that if the concentration of hydrogen is insufficient, clusters are not formed and hence hardening is not observed but softening occurs. The present experiments clearly demonstrate a macroscopic hardening of copper charged cathodically at higher current densities and charging times while no softening of the charged surfaces was observed during even lower cathodic charging conditions. Cathodic charging of hydrogen has been observed to produce dislocations near the charging surface in titanium-molybdenum alloys (12). It was concluded that the dislocations resulted from the hydrogen concentration gradient between the charging surface and the sample bulk. The maximum elastic stress that can result from such a phenomenon occurs at the surface and is directly proportional to the surface concentration (13). This elastic stress is calculated from elastic equilibrium; yielding would likely occur which would reduce the stress considerably.

*- Recovery of hardness during ageing*

It is well recognized that hydrogen diffusion is affected by defects such as vacancies, dislocations, grain boundaries, interfaces and voids, all of which may be classified as traps. The diffusion of hydrogen is fairly fast even at room temperature, the desorption of hydrogen from metals takes a much longer time than its absorption because of the trapping of hydrogen in these structural imperfections. Thereby, additional microhardness measurements were undertaken at certain time intervals after charging to assess the reversibility of the severe hardness produced by charging due to the diffusion of hydrogen out of copper specimens. Figure 11 shows how the microhardness recovered fully or partially during natural ageing for various charging conditions.

The microhardness of the copper specimens was found to decrease steadily after removal from the charging bath. The specimens charged at  $50\text{mA}\cdot\text{cm}^{-2}$  current density or higher current densities and those charged for 48 hours or longer did not fully recover to the original microhardness during natural ageing. However, the specimens charged at lower current density (i.e.  $25\text{mA}\cdot\text{cm}^{-2}$ ) and those for shorter charging time (i.e. 12 hours) showed completely reversible behavior after the natural ageing.

It was observed that the microhardness of the specimens charged for longer charging time took longer time of ageing to decrease rapidly than those charged at higher current density. As shown in figure 12, beyond 80 hours ageing, the microhardness of the specimens charged at higher current densities decreased rapidly while the microhardness of the specimens charged for longer charging time decreased rapidly after 100 hours of ageing as shown in the same figure.

These results revealed that the desorption of hydrogen from the specimens charged for longer times took longer time of ageing than from those charged at higher current density. This may be due to the different penetration depth of diffused hydrogen during the two cathodic charging conditions. The hydrogen atoms generated during the cathodic charging for longer times penetrated deeply into the specimen than those at higher current densities.

## Conclusions

1. Cathodic hydrogen charging was found to reduce the ductility and ultimate tensile strength of copper. These parameters are decreased with increasing the current density and charging time.
2. The fracture surfaces of the charged specimens consisted of mixed fracture mode, intergranular fracture was found in the outer periphery of the cross sectional areas while ductile fracture was observed in the center of the fracture surfaces of the hydrogen charged copper specimens.
3. Microhardness of copper was increased considerably by cathodic hydrogen charging. The increase depends on both the current density and charging time. Cathodic charging at lower cathodic current densities or lower charging times did not affect the hardness of copper.
4. Cathodic hydrogen charging for longer times produced a more severely hardened surface region than that of higher current densities when the charging time has maintained at a constant value.
5. The depth of the hardened region was increased with both the cathodic current density and charging time. However, charging for longer times produced more increase of the depth of hardening across the thickness of the charged copper specimens than that of higher current densities.
6. During natural ageing, hardness was recovered fully or partially, depending on the cathodic hydrogen charging applied to the copper specimens. The specimens charged at higher current density and those for longer time of charging did not fully recover to the original microhardness during natural ageing.

## REFERENCES

- [1] J.W. Watson, Y.Z. Shen and M. Meshii, *Metall. Trans. A*, Vol. 19A (1988), p. 2299.
- [2] A. Kimura and H.K. Birnbaum, *Acta Metall.* Vol. 35 (1987), p. 1077.
- [3] C. Panagopoulos and P. Papapanayiotou, *J. Mater. Sci.* Vol. 30 (1995), p. 3450.
- [4] A. Kimura and H. Kimura, *Mater. Sci. Eng.*, Vol. 77 (1986), pp. 75-83.
- [5] A. Iost and J.B. Vogt, *Scr. Mater.*, Vol. 37, 10 (1997), pp. 1499-1504.
- [6] T. Matsumoto, J. Easman and H.K. Birnbaum, *Scr. Metall.*, Vol. 15 (1987), pp. 1033-1037.
- [7] I.M. Robertson and H.K. Birnbaum, *Acta Metall.*, Vol. 34 (19886), pp. 353-366.
- [8] T. Tabata and H.K. Birnbaum, *Scr. Metall.*, Vol. 17 (1983), pp. 947-950.
- [9] T. Tabata and H.K. Birnbaum, *Scr. Metall.*, Vol. 18 (1984), pp. 231-236.
- [10] H. Matsui, H. Kimura and S. Moriya, *Mater. Sci. Eng.*, Vol. 40 (1979), p. 207.
- [11] S. Moriya, H. Matsui and H. Kimura, *Mater. Sci. Eng.*, Vol. 40 (1979), p. 217.
- [12] J.P. Hirth, *Metall. Trans., A*, Vol. 11A (1980), pp. 861-890.
- [13] B. Ladna and H.K. Birnbaum, *Acta Metall.*, Vol. 35 (1987), p. 2537-2542.

**APPENDIX**

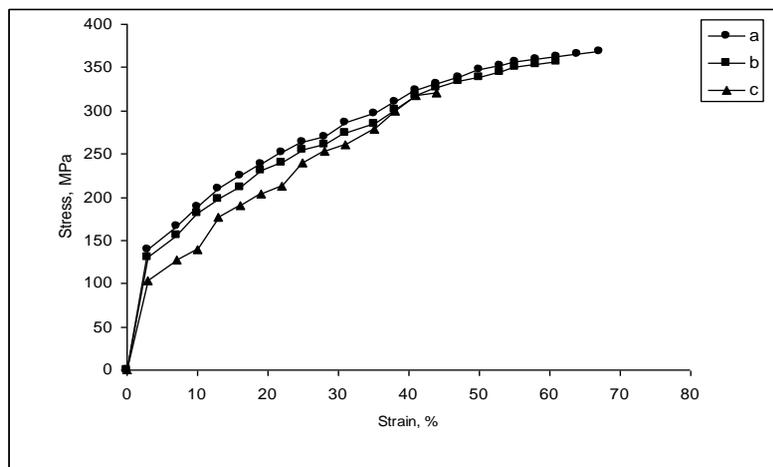


Figure 1 Engineering stress-strain curves for copper tensile specimens at room temperature. (a) uncharged specimen, (b) specimen charged at  $15\text{mA}\cdot\text{cm}^{-2}$ , (c) specimen charged at  $65\text{mA}\cdot\text{cm}^{-2}$  for 24 hrs.

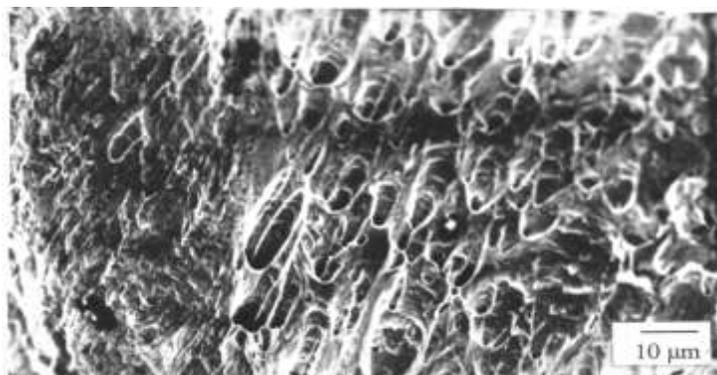


Figure 2 Fracture surface of the uncharged copper tensile specimen.

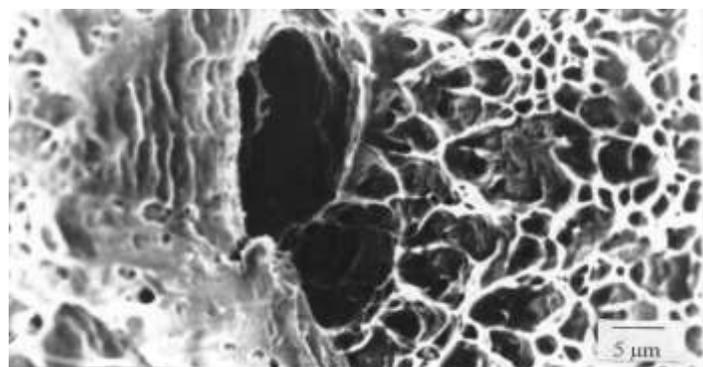


Figure 3 Fracture surface of the charged copper specimen cathodically hydrogen charged at  $15\text{mA}\cdot\text{cm}^{-2}$  current density for 24 hrs .

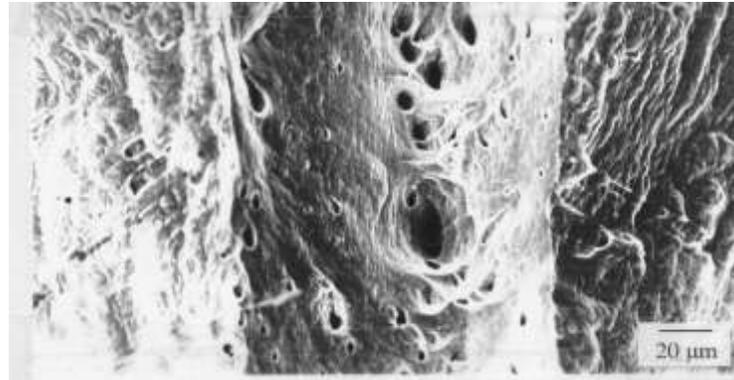
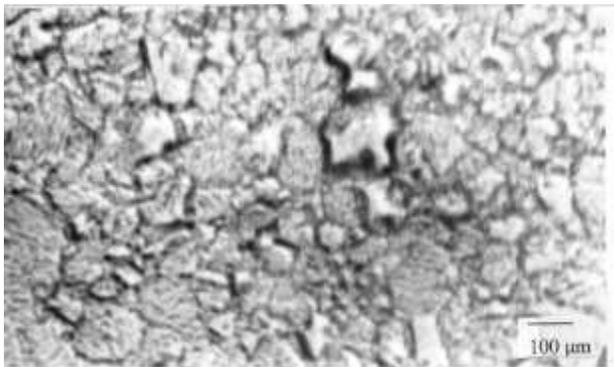
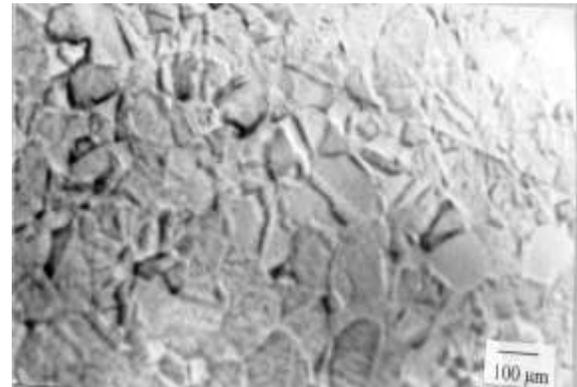


Figure 4 Fracture surface of the charged copper specimen cathodically hydrogen charged at  $65\text{mA}\cdot\text{cm}^{-2}$  current density for 24 hrs.



(a)



(b)

Figure 5 Cross-sectional views of the copper specimens charged at the current densities of (a)  $15\text{mA}\cdot\text{cm}^{-2}$ , (b)  $65\text{mA}\cdot\text{cm}^{-2}$  and fractured in tension.

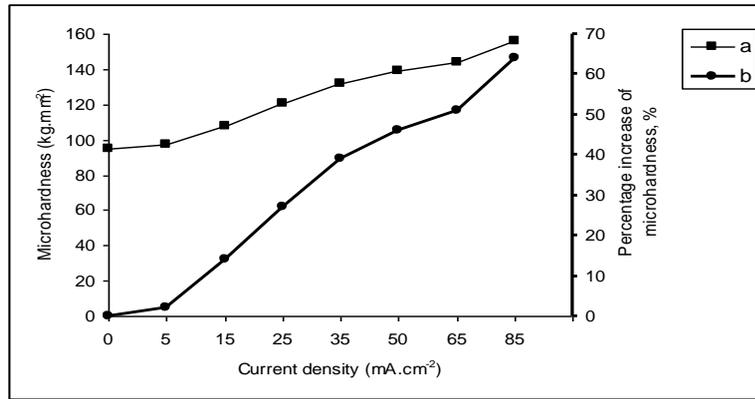


Figure 6 Effect of current density for a constant charging time on Vickers microhardness: (a) Surface Microhardness, (b) Percentage increase of surface microhardness of copper (Bold curve).

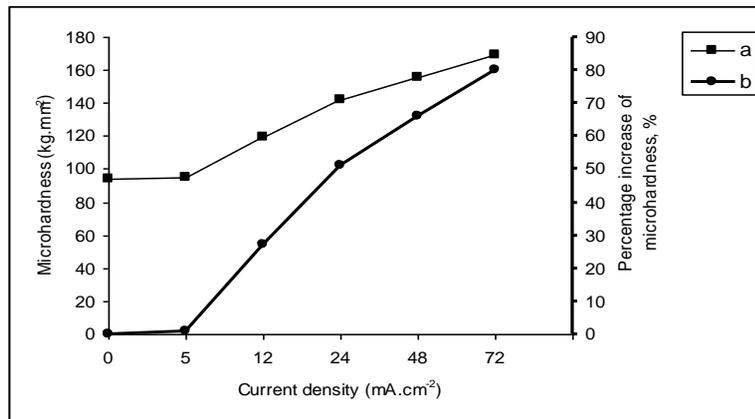


Figure 7 Effect of charging time at a constant current density on Vickers microhardness: (a) Surface Microhardness, (b) Percentage increase of surface microhardness of copper (Bold curve).

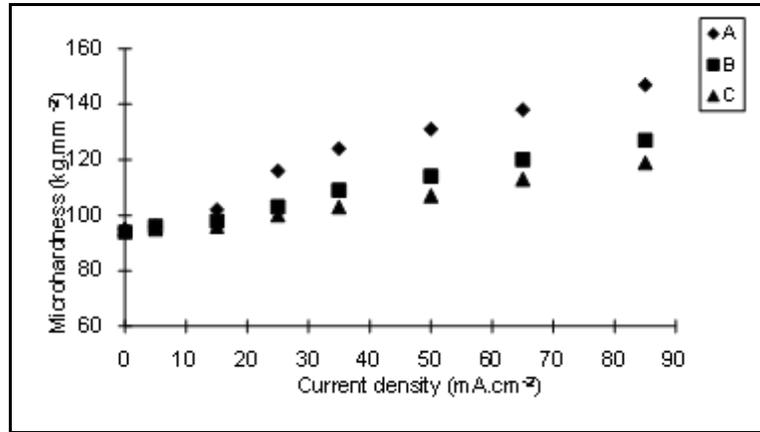


Figure 8 Effect of current density for a constant charging time on the severity of microhardness across the thickness (perpendicular to tubing axis) of copper specimens, (A) the near-charged surface, (B) and (C) the interior surfaces.

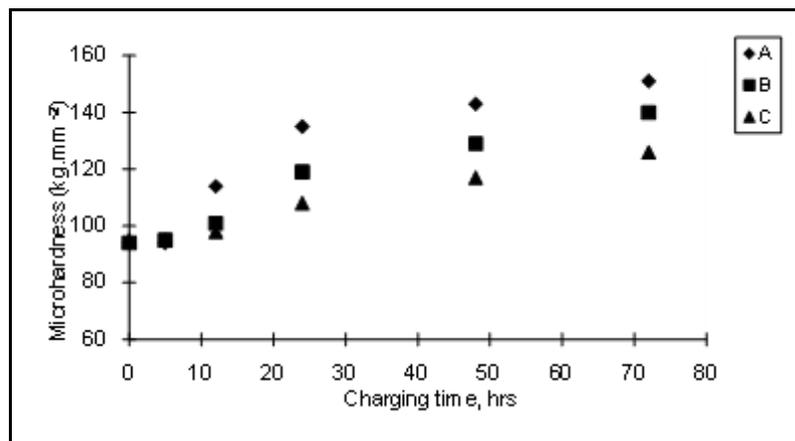


Figure 9 Effect of charging time for a constant current density on the severity of microhardness across the thickness (perpendicular to tubing axis) of copper specimens, (A) the near-charged surface, (B) and (C) the interior surfaces.

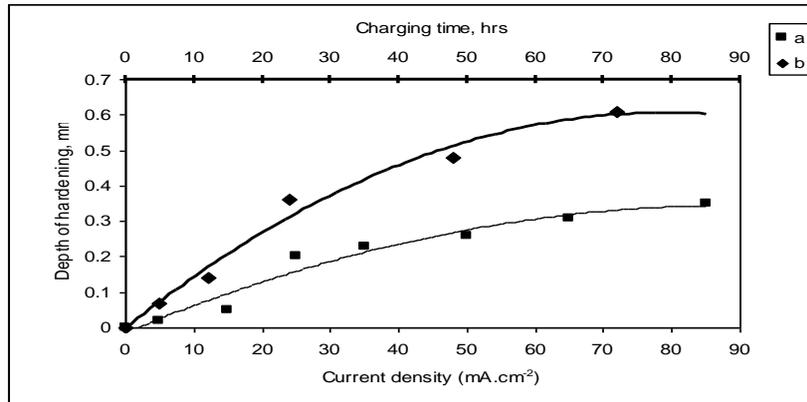


Figure 10 Effect of current density for a constant charging time (a) and charging time at a constant current density (Bold curve) (b) on the depth of hardening across the thickness (perpendicular to tubing axis) of copper specimens.

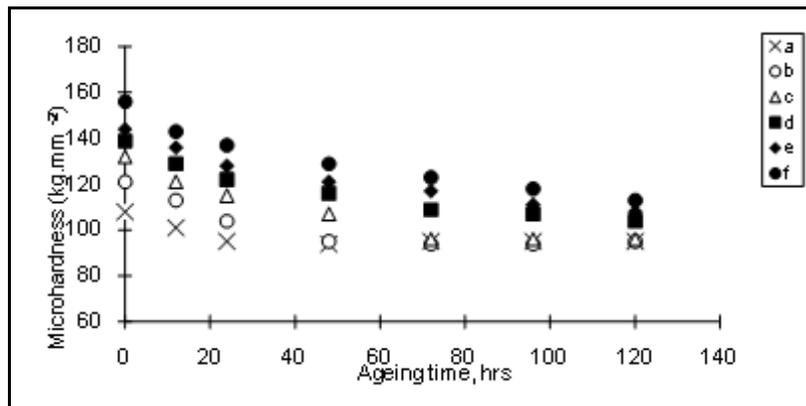


Figure 11 Effect of natural ageing on microhardness recovery after hydrogen charging at (a) 15mA.cm<sup>-2</sup>, (b) 25mA.cm<sup>-2</sup>, (c) 35mA.cm<sup>-2</sup>, (d) 50mA.cm<sup>-2</sup>, (e) 65mA.cm<sup>-2</sup>, (f) 85mA.cm<sup>-2</sup>, current densities for a constant charging time.

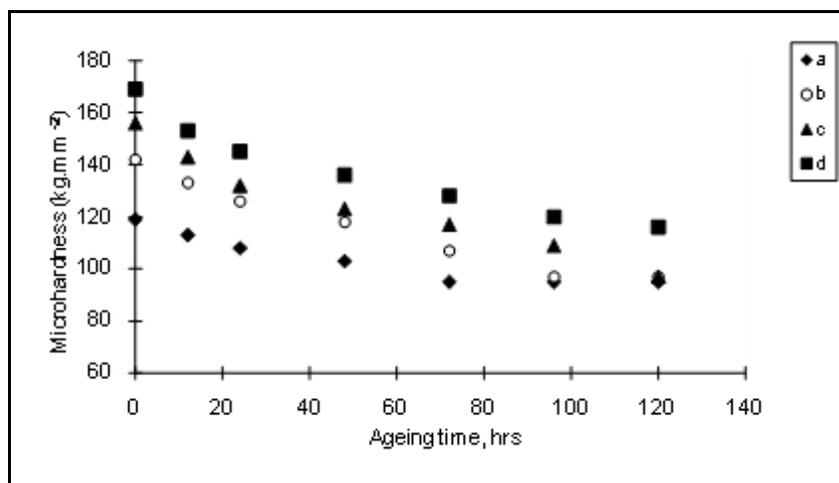


Figure 12 Effect of natural ageing on microhardness recovery after hydrogen charging at a constant current density for (a) 12 hrs, (b) 24 hrs, (c) 48 hrs, (d) 72 hrs.

Table 2 Mechanical properties of copper specimens at room temperature. The strain rate was  $2.4 \times 10^{-4} \text{ S}^{-1}$ . The charging time was 24 hrs.

Current Density, (mA.cm <sup>-2</sup> )	Ultimate Tensile Strength, (MPa)	Elongation, (%)
0	368	67
15	357	61
65	321	44

**Received: August 11, 2013**