

## Effect of Cathodically Charged Hydrogen on the Microhardness of Pure Copper

Ghazi S. AL-Marahleh and Amjad S. El-Amoush

Al-Balqa' Applied University, Materials and Metallurgical Engineering Department  
Salt-19117-Jordan

**Abstract:** The effect of hydrogen on the microhardness of pure copper was investigated after experiments conducted on specimens that hydrogen charged under different cathodic charging conditions. 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.

**Key words:** Hydrogen Charging, Pure Copper, Microhardness

### INTRODUCTION

The effect of hydrogen on hardness of the metallic materials has been reported by several investigators. Lost and Vogt [1] 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 [1]. Panagopoulos and Papapanayiotou [2] found that cathodic hydrogen charging of Al-4Zn-1Mg alloy produced major surface hardening. The last investigators 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-4 Zn-1 Mg decreased during natural ageing. They concluded that the surface layer did not recover to its prior-to-charging hardness with the time passed after charging.

The objective of this study was to determine the effect of cathodic hydrogen charging on microhardness of pure copper. 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. Furthermore, the inhomogenous distribution of cathodically hydrogen charged within the tested specimens is investigated using the same manner.

### MATERIALS AND METHODS

The material used in this investigation was pure copper sheet of 1mm thickness. A number of specimens were cut from this sheet with dimensions of 3x1 cm. 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 repolishing 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 1.5 V using a stainless steel cathode in a solution of 40 vol.% orthophosphoric and 60 vol.% 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 two graphite anodes, 10x5x1 cm<sup>3</sup> which were positioned on both side of a certain gage section area of the specimen. This positioning provides a charging of the specimen on both the front and back surfaces. 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 with a certain gage section area of the specimen exposed to the electrolytic solution while the rest of the specimen was covered with shielding tape.

The electrolytic solution contains 75% (volume) methanol, 22.4% (volume) distilled water, 2.6% (volume) sulphuric acid and 10 mg per liter arsenic

trioxide to inhibit hydrogen recombination at the surface. Constant current densities between 5 and 85 mA cm<sup>-2</sup> were applied to the specimens. The hydrogen charging time varied from 5 up to 72 h. The experiments were performed at room temperature. The specimen surface area in contact with the electrolyte was 4 cm<sup>2</sup>.

The microhardness was measured immediately after cathodic hydrogen charging and after various time intervals. Microhardness measurements were made across and along the width, length and thickness of the specimens as shown in Fig. 1. Indentation measurements were carried out with a Vickers indenter a 25 g load for 20 sec. Each measurement was the average of three indentations.

**RESULTS AND DISCUSSION**

**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 [2]. 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 [2]. The effect of the cathodic current density on surface microhardness of copper is shown in Fig. 2. It is clear that the hardness increased rapidly after charging at approximately 25 MA cm<sup>-2</sup>. Cathodic charging at lower cathodic current densities showed no change in the hardness as shown in this Fig. 2. 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 percentage increase of microhardness as a function of cathodic current density (the charging time was maintained at a constant value) is calculated referring to the uncharged specimen. The results of this semiquantitative study of the percentage increase of microhardness are shown in Fig. 3. As can be seen from this Fig. 3 the maximum percentage increase of microhardness  $\Delta(MH)_{I_{CD}}$  is 59%. The effect of the charging time on surface microhardness of copper is shown in Fig. 4. It is clear that the hardness increased rapidly after approximately 10 h charging. Cathodic charging for shorter time showed also no change in the hardness as shown in this Fig. 4. Thus the

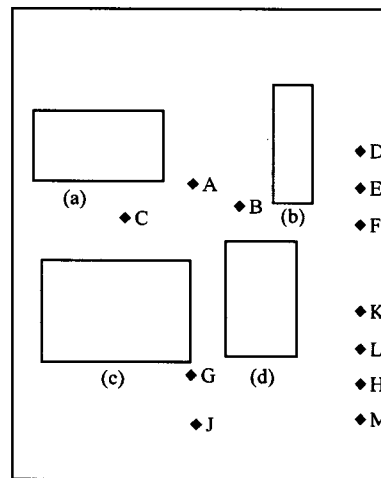


Fig. 1: Schematic Diagram of the Sections for Measuring the Microhardness. The Measurements were Conducted (a) Across, (b) Along the Thickness, (c) Across the Width and (d) Along the Length of the Specimens

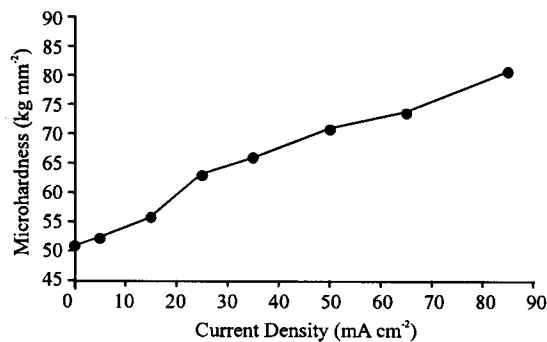


Fig. 2: Effect of Current Density at a Constant Charging Time on Surface Vickers Microhardness of Copper

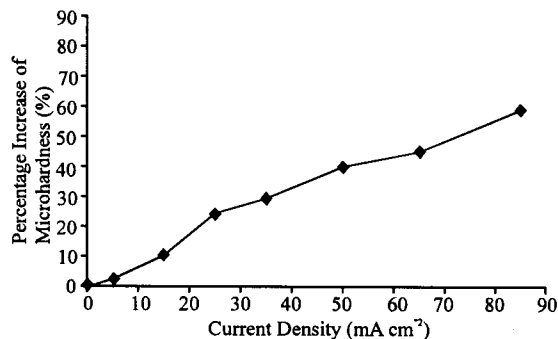


Fig. 3: Percentage Increase of Surface Vickers Microhardness of Copper as a Function of Current Density for a Constant Charging Time

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 shown in Fig. 5. As can be seen from this Fig. 5, the maximum percentage increase of microhardness  $\Delta(MH)_{t_{CH}}$  is 71%. However, in contrast with the  $\Delta(MH)_{I_{CD}}$ , the  $\Delta(MH)_{t_{CH}}$  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 diffusion of hydrogen into the specimen, while the diffusion of hydrogen during the charging at higher current densities might be limited to the surface region.

**Depth of Hardening:** Additional microhardness measurements were made across and along the width, length and thickness 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 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 in Fig. 1a respectively. The severity of microhardness on these areas as a function of current density and charging time are shown in Fig. 6 and 7, 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 of the copper specimens is shown in Fig. 8. Based on the results shown in this Fig. 8, a charging at cathodic current density of  $15 \text{ mA cm}^{-2}$  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  $25 \text{ mA cm}^{-2}$  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  $25 \text{ mA cm}^{-2}$  current

density. The further increase in the current density resulted in an increase the depth of the hardened surface region as shown in Fig. 8.

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.

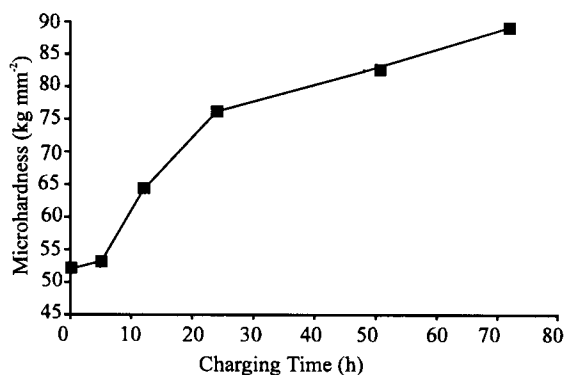


Fig. 4: Effect of Charging Time at a Constant Current Density on Surface Vickers Microhardness of Copper

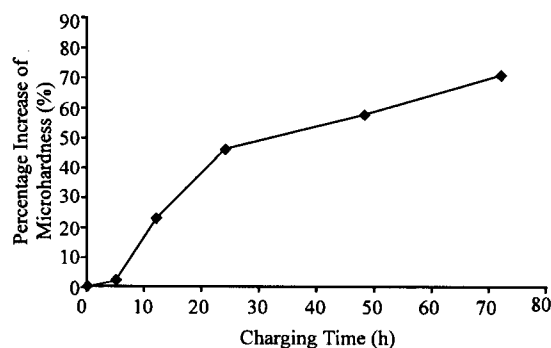


Fig. 5: Percentage Increase of Microhardness as a Function of Charging Time at a Constant Current Density

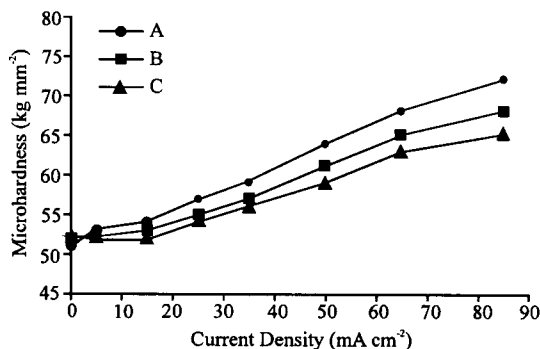


Fig. 6: Effect of Current Density for a Constant Charging Time on the Severity of Microhardness Across the Thickness of Copper Specimen. (a) Area A, (b) Area B and (c) Area C In Fig. 1

Microhardness measurements, which were conducted on the near-charged surface layer of the copper specimen charged for 12 h (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 h 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 h charging. However, charging beyond 40 h 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 Fig. 9.

The microhardness measurements that have been made along the specimen thickness revealed also a severely hardened region on the lower area (D in Fig. 1b) and a less severely hardened region on the middle and upper areas (E and F in the same Fig. , respectively) of the charged surface of the copper specimen as compared to the uncharged specimen. It was found from the test results that the severity of the hardened region increased also with either the cathodic current density or charging time.

The effect of the cathodic current density on the severity of hardening of the areas D, E and F along the thickness of the charged surface of copper specimens is shown in Fig. 10. Based on these experimental findings, it was observed that charging at cathodic current densities of 25 mA cm<sup>-2</sup> (the charging time was maintained at a constant value) showed a severe hardening on the lower areas (D) and a less severe on the middle area, however, no comparable hardening on the upper area of the charged surface of copper specimen was found by the microhardness measurements.

These results indicated that the lower area occluded the larger amount of hydrogen while the middle areas occluded smaller amount of hydrogen. However the amount of hydrogen occluded on the upper area during this charging condition was too small to affect the hardness. A cathodic charging condition of 35 mA cm<sup>-2</sup> current density showed a higher hardness on both lower and middle areas. Furthermore, the microhardness measurements, which were conducted on the upper area revealed a slight hardening due to hydrogen. The above results showed that the further increase in the current density resulted in an increase of the microhardness on the lower, middle and upper areas as shown in Fig. 10. Based on these results, it can be suggested that higher densities, larger amount of hydrogen occluded in the specimens and hence higher hardness.

The effect of the charging time on the severity of hardening of the areas D, E and F is shown in Fig. 11.

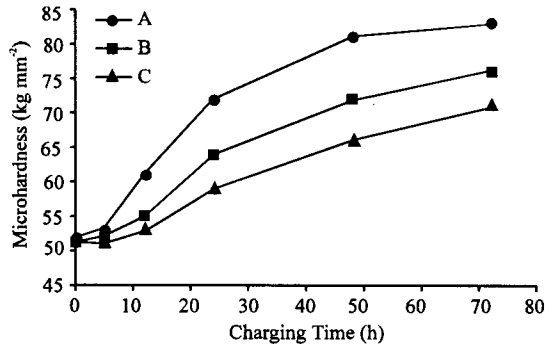


Fig. 7: Effect of Charging Time for a Constant Current Density on the Severity of Microhardness Across the Thickness of Copper Specimen (a) Area A, (b) Area B and (c) Area C In Fig. 1

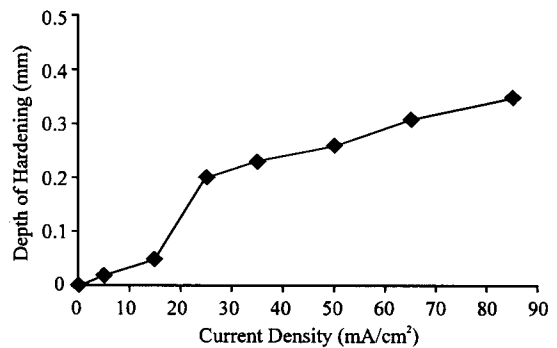


Fig. 8: Effect of Cathodic Current Density for a Constant Charging Time on the Depth of Hardening Across the Thickness of Copper Specimens

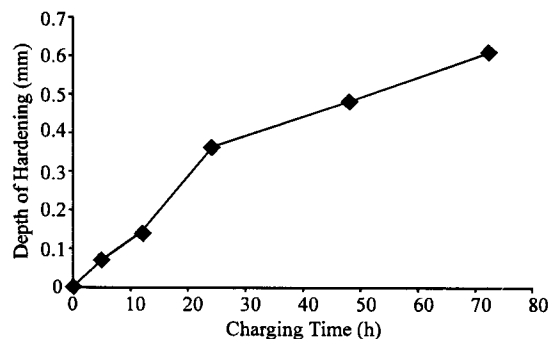


Fig. 9: Effect of Charging Time at a Constant Current Density on the Depth of Hardening Across the Thickness of Copper Specimens

As shown in Fig. 11, cathodic charging for 12 h (the current density was maintained at a constant value) produced a severe hardening on the lower areas (G) and a less severe on the middle area (H), however, in the contrast with the upper area (J) charged by higher cathodic current density condition, a slight hardening

on this area was observed when the specimen charged for longer time. The severity of hardening observed along the specimen thickness can be explained also by the different saturation levels achieved by cathodic charging for longer times. As reported previously the lower area occluded charging time the larger amount of hydrogen and smaller amount of hydrogen was occluded by the middle areas, however as revealed by the microhardness measurements conducted across the specimen thickness, the upper area exhibited hardening during cathodic charging for longer times. Thus it seems reasonable to confirm for this finding that the cathodic charging for longer times caused more hydrogen atoms to diffuse into the specimens, resulting in the hardening of whole areas along the section of the copper specimen, as compared with the higher cathodic current density conditions. Further charging showed a higher hardness on the lower, middle and upper areas. The microhardness measurements that have been made across the width of the charged specimen revealed severely hardened regions on all the areas (G, H and J in Fig. 1c). This experimental result may indicate that the cathodically charged hydrogen distributed homogeneously across the width of the copper specimen.

Consequently the microhardness measurements that have been made along the length of the charged specimen revealed also a severely hardened region on the lower area (K in Fig. 1d) and a less severely hardened region on the middle and upper areas (L and M in the same figure, respectively) of the charged surface of the copper specimen as compared to the uncharged specimen. Figure 12 shows the effect of the cathodic current density on the severity of hardening of the areas K, L and M along the length of the charged surface of copper specimens. The effect of the charging time on the severity of hardening of these areas is shown in Fig. 13. It is clearly seen from these figures that the severity of the hardened region increased also with the cathodic current density and charging time.

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 [3]. 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 [4, 5] and iron [6, 7] 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

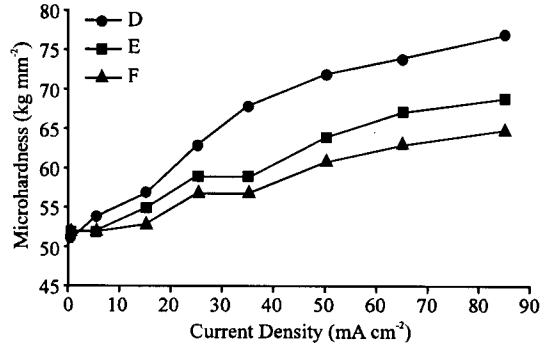


Fig. 10: Effect of Current Density for a Constant Charging Time on the Severity of Hardening of the Areas D, E and F (Fig. 1b) along the Thickness of the Charged Surface of Copper Specimens

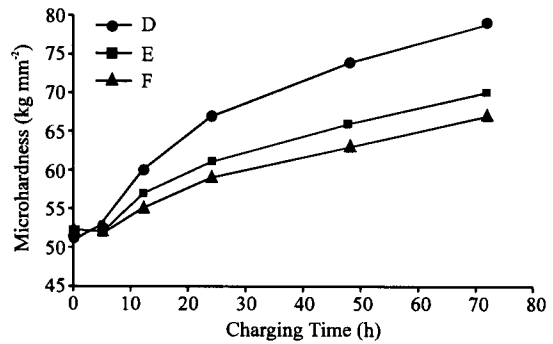


Fig. 11: Effect of Charging Time at a Constant Current Density on the Severity of Hardening of the Areas D, E and F (Fig. 1b) along the Thickness of the Charged Surface of Copper Specimens

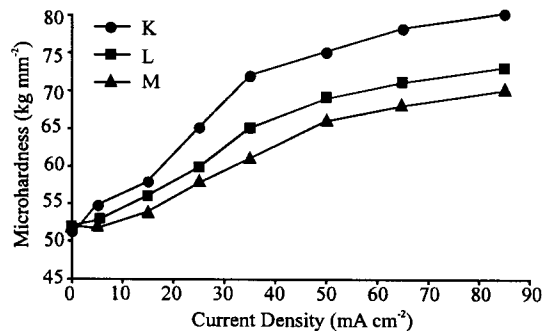


Fig. 12: Effect of Current Density for a Constant Charging Time on the Severity of Hardening of the Areas K, L and M along the Length of the Charged Surface of Copper Specimens

hydrogen [8]. 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

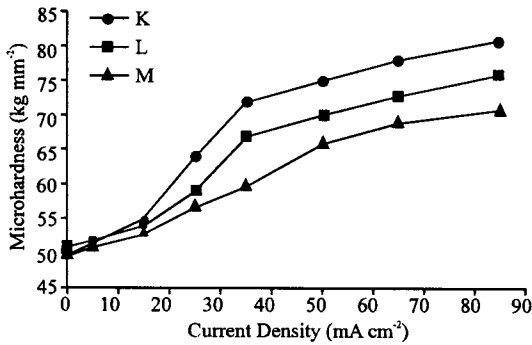


Fig. 13: Effect of Charging Time at a Constant Current Density on the Severity of Hardening of the Areas K, L and M along the Length of the Charged Surface of Copper Specimens

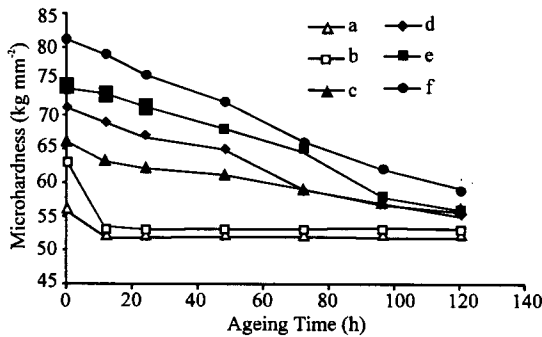


Fig. 14: Effect of Natural Ageing on Microhardness Recovery After Hydrogen Charging at (A) 15 mA cm<sup>-2</sup>, (B) 25 mA cm<sup>-2</sup>, (C) 35 mA cm<sup>-2</sup>, (D) 50 mA cm<sup>-2</sup>, (E) 65 mA cm<sup>-2</sup>, (F) 85 mA cm<sup>-2</sup>, Current Densities for a Constant Charging Time

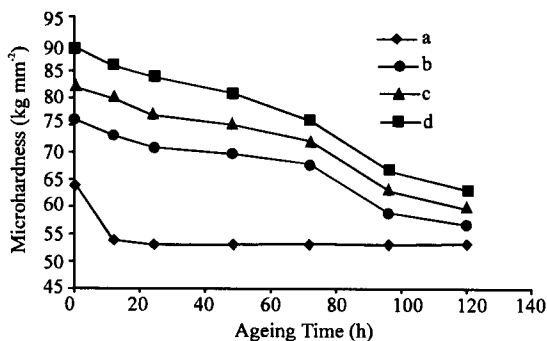


Fig. 15: Effect of Natural Ageing on Microhardness Recovery after Hydrogen Charging at a Constant Current Density for (a) 12 h, (b) 24 h, (c) 48 h, (d) 72 h

considered to be due to the interaction of hydrogen clusters with the edge component of dislocations [9]. It is concluded that if the concentration of hydrogen is insufficient, clusters are not formed and hence hardening is not observed but softening occurs [10].

The 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 [11]. 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 [12]. 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 hardening produced by charging due the diffusion of hydrogen out of copper specimens. Figure 14 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 85 mA cm<sup>-2</sup> current density and those charged for 48 h did not fully recover to the original microhardness during natural ageing. However, the specimens charged at lower current density (i.e. 25 mA cm<sup>-2</sup>) and those for shorter charging time (i.e. 12 h) showed completely reversible behaviour 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 Fig. 15, beyond 70 h 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 h of ageing as shown in the Fig. 15.

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.

### CONCLUSION

- \* 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.
- \* 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.
- \* 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. The lower areas along the specimen thickness and along the length showed a higher hardness than that of the middle and upper areas. These results indicated that the lower area occluded the larger amount of hydrogen while the middle areas occluded smaller amount of hydrogen.
- \* 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. However, the specimens charged at lower current density and those for shorter charging time showed completely reversible behavior after the above period of 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.

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