

# Cathodic hydrogen charging and mechanical properties of copper

C. N. PANAGOPOULOS, N. ZACHAROPOULOS

Laboratory of Physical Metallurgy, National Technical University of Athens,  
Zografou Campus, 15773, Athens, Greece

The influence of cathodic hydrogen charging on some mechanical properties of copper was studied. Hydrogen charging was found to decrease both the ultimate tensile strength and the failure strain of copper. The surface layers of copper were hardened, but they recovered to their prior hardness with time passed after hydrogen charging.

## 1. Introduction

Hydrogen may be introduced into metallic materials during casting, heat treatment, acid pickling, electroplating, welding and corrosion processes. Hydrogen is present in metallic material in the form of small interstitial atoms, which can move rapidly either by diffusion or by transportation through mobile line defects. The influence of hydrogen is closely related to the metallic material's strength, its microstructure, the applied stress, the percentage of prior cold work and the degree of segregation of impurities at the grain boundaries [1].

The most recent publications dealing with cathodic hydrogen charging and the mechanical behaviour of some metallic materials are given below.

Kim and Byrne [2] examined hydrogen–defect interaction in the Cu–Al binary system, and found that this interaction depends strongly on the stacking fault energy of the system. The same investigators performed annealing studies of copper and copper alloys with 4 and 8 wt % aluminium, and observed that hydrogen trapping started around 60–100 °C and that detrapping occurred from 110 °C and above.

Kimura and Birnbaum [3] examined the influence of cathodic hydrogen charging on the mechanical behaviour of nickel and nickel–carbon alloys, and observed that cathodic charging can cause both softening and hardening of those metallic materials.

Cathodic hydrogen charging of pure aluminium was found to decrease ductility, and increase the yield and ultimate tensile stress of those materials by Watson and co-workers [4].

Bond *et al.* [5] studied the effect of cathodic hydrogen charging on the deformation behaviour of pure aluminium, and noticed that hydrogen increases the dislocation mobility and reduces the flow stress of aluminium.

Finally, Shim and Byrne [6] showed that the mechanical aspects of hydrogen embrittlement in ultrahigh strength 4340 steel include strength degradation, fracture mode and microstructural changes.

The purpose of this study is to investigate the effect

of cathodic hydrogen charging on some mechanical properties of pure copper.

## 2. Experimental procedure

The material used was commercial copper (99.9%) supplied as a cold rolled sheet. The samples were annealed for 1 h at 350 °C, and were immediately subjected to chemical etching in a solution of 33.3% nitric acid, 33.3% phosphoric acid and 33.3% acetic acid, prior to cathodic hydrogen charging.

Cathodic charging was carried out in a solution of 75% methanol, 22.4% water, 2.6% sulfuric acid, and contained 10 mg l<sup>-1</sup> arsenic trioxide as a hydrogen recombination inhibitor. The specimens were charged on both the front and back surfaces, using graphite anodes. The charging current densities employed were in the range of 10–100 mA cm<sup>-2</sup> for the tensile tests, and 50–150 mA cm<sup>-2</sup> for the microhardness tests; while the charging time was varied from 3 to 36 h and from 6 to 24 h, respectively.

Mechanical testing was carried out immediately after charging to minimize the loss of hydrogen. The gauge sections for the tensile tests were: 50 × 10 × 0.8 mm. The tension tests were performed at a strain rate of 4 × 10<sup>-3</sup> s<sup>-1</sup>. One series of testing, however, involved the variation of strain rate from 4 × 10<sup>-4</sup> s<sup>-1</sup> to 2 × 10<sup>-2</sup> s<sup>-1</sup>. Microhardness testing was made with a Vickers indenter using a 25 gr load for 20 s. Each measurement was the average of six indentations.

## 3. Results and discussion

### 3.1. Tension tests

Fig. 1 shows the influence of cathodic hydrogen charging on the engineering stress–strain curve of copper. As noticed, hydrogen charging of copper decreases the ultimate tensile strength and the failure strain of this metallic material.

The effects of cathodic hydrogen charging on the ultimate tensile strength (UTS) of copper are

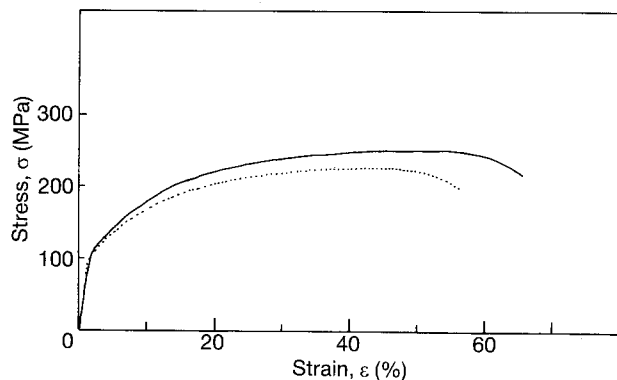


Figure 1 Engineering stress-strain curves for copper which was (a) (—) strained and (b) (---) charged for 12 h at  $25 \text{ mA cm}^{-2}$  and then strained.

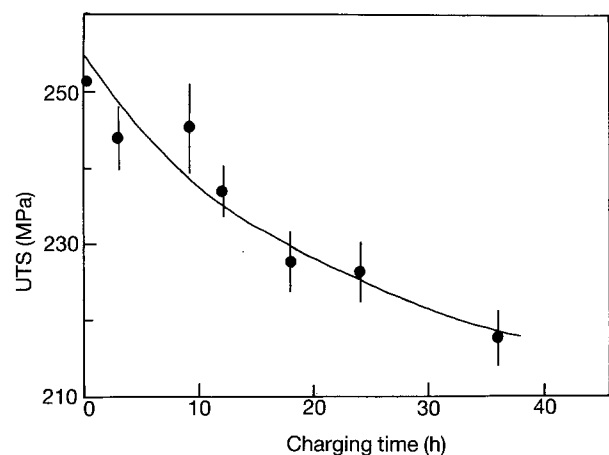


Figure 2 Effect of charging time on the ultimate tensile stress (UTS) of copper at a current density of  $25 \text{ mA cm}^{-2}$ .

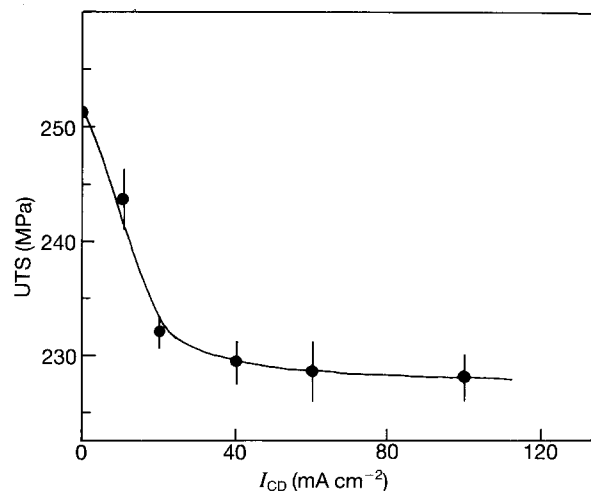


Figure 3 Effect of charging current density ( $I_{CD}$ ) on the ultimate tensile stress (UTS) of copper charged with hydrogen for 3 h.

displayed in Figs 2 and 3. In the case of variable charging time, Fig. 2, it can be seen that the ultimate tensile strength of copper decreases steadily, although with descending rate. Increasing the charging current density ( $I_{CD}$ ) has the same effect on the ultimate tensile strength, Fig. 3, at least up to  $60 \text{ mA cm}^{-2}$ , where saturation seems to occur. The abrupt decrease of

ultimate tensile strength versus current density in the range  $0\text{--}20 \text{ mA cm}^{-2}$  (as compared with the steady decrease of ultimate tensile strength versus charging time) might be explained by the fact that the introduction of hydrogen into the copper involves electric field assisted absorption and diffusion. Thus, up to the saturation point, hydrogen diffusion into the copper is mainly controlled by the applied electric field and, hence, hydrogen diffusion into the copper is mainly controlled by the charging time.

Figs 4 and 5 display the effect of hydrogen charging on the failure strain ( $\epsilon_{fr}$ ) of deformed copper specimens. Failure strain values drop steadily with increasing charging time, Fig. 4. Plotted against current density ( $I_{CD}$ ), Fig. 5, failure strain ( $\epsilon_{fr}$ ) follows a steep drop in value and then appears to saturate, as in the case of the ultimate tensile strength of hydrogen charged copper.

Fig. 6 shows that the ultimate tensile strength (UTS) of hydrogen charged copper specimens increases with increasing strain rate ( $\dot{\epsilon}$ ); whereas, Fig. 7 shows the failure strain ( $\epsilon_{fr}$ ) of the same specimens to decrease with increasing strain rate ( $\dot{\epsilon}$ ).

### 3.2. Microhardness tests

Microhardness measurements were conducted on the surface after charging revealed an increase in surface hardness in relation to both charging time, Fig. 8, and

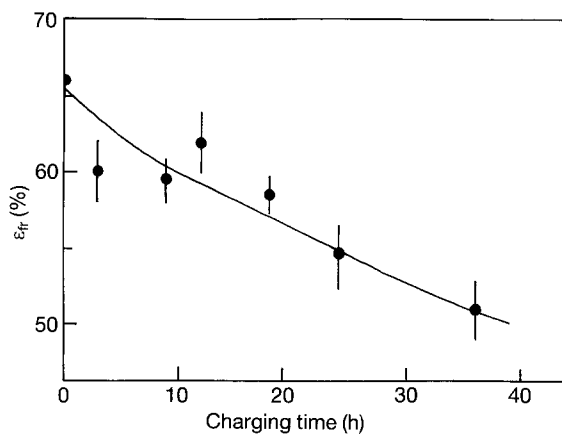


Figure 4 Effect of charging time on the failure strain ( $\epsilon_{fr}$ ) of copper at a current density of  $25 \text{ mA cm}^{-2}$ .

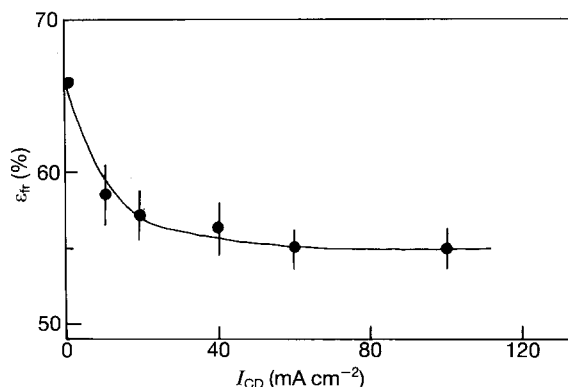


Figure 5 Effect of charging current density ( $I_{CD}$ ) on the failure strain ( $\epsilon_{fr}$ ) of copper charged with hydrogen for 3 h.

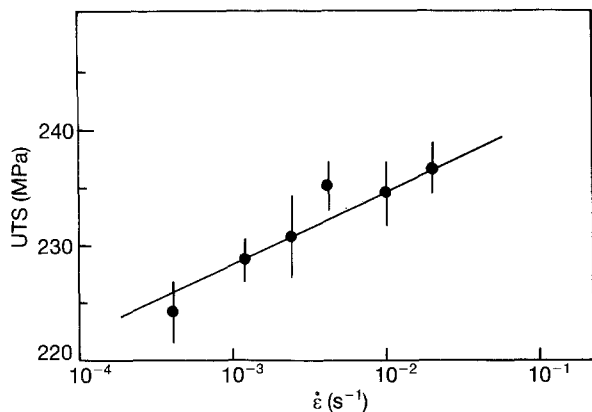


Figure 6 Effect of strain rate ( $\dot{\epsilon}$ ) on the ultimate tensile strength (UTS) of specimens charged for 3 h at  $25 \text{ mA cm}^{-2}$ .

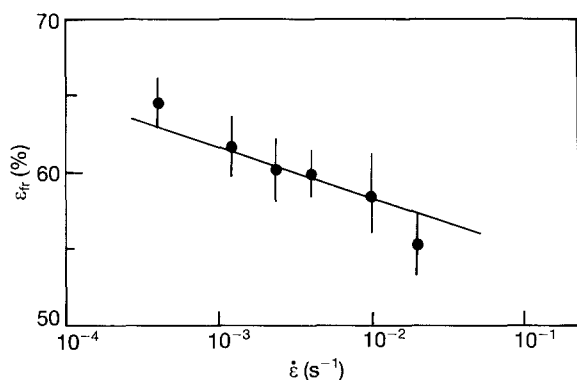


Figure 7 Effect of strain rate ( $\dot{\epsilon}$ ) on the failure strain ( $\epsilon_r$ ) of specimens charged for 3 h at  $25 \text{ mA cm}^{-2}$ .

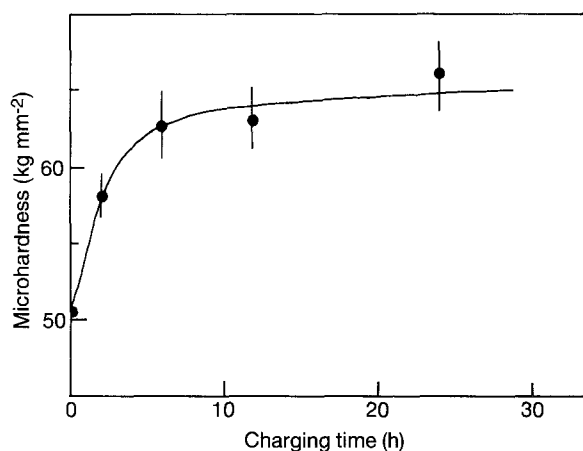


Figure 8 Effect of hydrogen charging time on surface Vickers microhardness of copper ( $40 \text{ mA cm}^{-2}$  current density).

current density ( $I_{CD}$ ), Fig. 9. Microhardness appeared to reach a saturation level with increasing current density, while no such saturation was apparent on the effect of charging time.

The results of the microhardness tests, indicating surface hardening, may be attributed to solute hydrogen and dislocation hardening of the surface region [4]. Dislocations may be generated by the hydrogen concentration gradient, but with increasing difficulty,

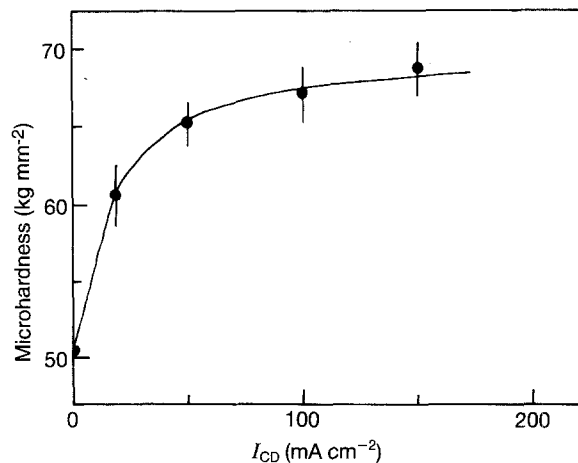


Figure 9 Effect of current density ( $I_{CD}$ ) on surface Vickers microhardness of copper (3 h charging time).

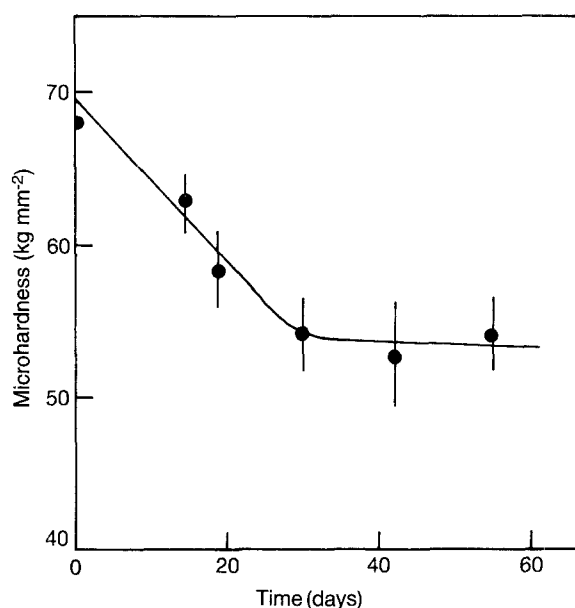


Figure 10 Effect of time passed after charging on the surface microhardness of a specimen charged for 24 h at  $40 \text{ mA cm}^{-2}$ .

due to increased resistance to new dislocation production by the existing dislocations.

The bulk effects of hydrogen charging, as displayed by the tension tests, point out that hardening is limited to a surface layer, and does not expand into the interior. The loss of strength observed during tensile testing is probably due to cracking caused by hydrogen on the surface of the specimens [6]. Grain boundaries, subgrain boundaries and dislocation pile-ups could act as crack-initiating sites.

Another explanation of the difference between localized surface effects and macroscopic bulk effects could be ascribed to different hydrogen-dislocation interaction for the two types of deformation. Indentations may result in the pinning of dislocations on hydrogen atmospheres, or to the conveyance of interstitial hydrogen, by moving dislocations to more effective sites for the generation of new dislocations [2]. Tensile tests may present conditions for enhanced dislocation mobility [7], leading to softening of the hydrogen charged copper.

Another mechanism that may cause softening of the material is a decrease in the effectiveness of other pinning points due to the presence of solute hydrogen [8]. According to this mechanism, when the concentration of hydrogen in the metal is equivalent or lower than that of another cause of dislocation movement restriction, solid solution softening due to hydrogen is observed. In the case of pure copper localized stress fields, dislocation pile-ups, interfaces or/and grain boundaries could act as limitations to dislocation movement.

The decrease in microhardness as a function of time passed beyond charging, indicates an outward diffusion of hydrogen. Surface hardness is reduced to prior-to-charging values after 30 to 40 days have lapsed after charging, as can be observed from Fig. 10.

Although the hydrogen concentration was not analysed quantitatively in the present study, the relative hydrogen content can be determined theoretically using the following equation [9], for a plate-like specimen:

$$M_t/M_\infty = 1 - \sum_{n=0}^{\infty} [8/(2n+1)^2 n^2] \times \exp[-D(2n+1)^2 n^2 t/L^2] \quad (1)$$

In the above equation,  $M_t/M_\infty$  is the relative hydrogen content in the copper specimen after charging; time,  $t$ ,  $D$ , is the diffusion coefficient of hydrogen in copper, and  $L$  is the specimen thickness, respectively. Using appropriate values for the diffusion coefficient of hydrogen in copper at room temperature ( $3.11 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ ) [10] and the specimen thickness ( $L = 0.8 \text{ cm}$ ), the plot of Fig. 11 was produced.

In order to establish an opinion on the susceptibility of copper to hydrogen embrittlement, the hydrogen embrittlement ratio

$$\text{Hydrogen embrittlement ratio (\%)} = [(\epsilon_0 - \epsilon_H)/\epsilon_0] \times 100 \quad (2)$$

(where  $\epsilon_0$  and  $\epsilon_H$  are the failure strains of uncharged and charged copper, Fig. 4, respectively) was calculated and plotted against the relative hydrogen content, Fig. 12. From the last figure, a noticeable sus-

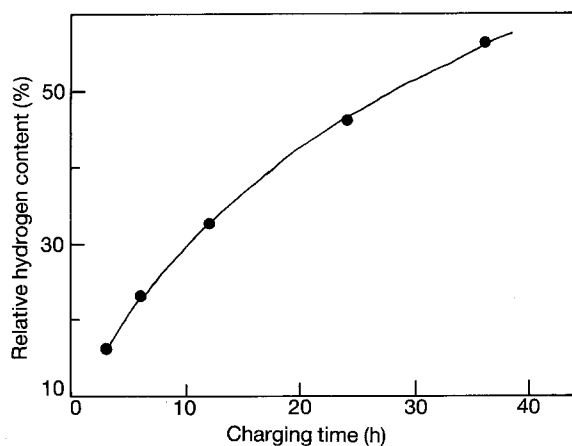


Figure 11 Relative hydrogen content as a function of charging time (25 mA cm<sup>-2</sup> current density).

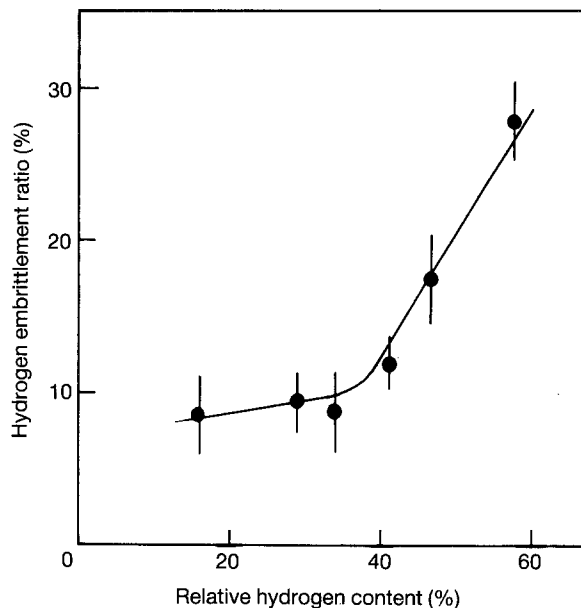


Figure 12 Hydrogen embrittlement ratio as a function of relative hydrogen content (25 mA cm<sup>-2</sup> current density).

ceptibility of copper to hydrogen embrittlement was observed.

#### 4. Conclusions

Hydrogen charging has been shown to decrease both the ultimate tensile strength and the failure strain of copper. The effects of current density appeared to saturate beyond a certain value, while no such saturation was noticed within the range of charging time. All specimens failed in a completely ductile manner. The surface of the material was hardened considerably, but this effect was restricted to a local character. The surface layer recovered to its prior-to-charging hardness with time passed after charging. A notable susceptibility of copper to hydrogen embrittlement was calculated.

#### References

1. V. KERLINS, "Metals handbook, Vol. 12, Fractography" 9th Edn (ASM, Metals Park, OH, 1987) p. 13.
2. J. J. KIM and J. G. BYRNE, *Mater. Sci. Engng* **74** (1985) 201.
3. A. KIMURA and H. K. BIRNBAUM, *Acta Metall.* **35** (1987) 1077.
4. J. W. WATSON, Y. Z. SHEN and M. MESHII, *Metall. Trans. A* **19** (1988) 2299.
5. G. M. BOND, I. M. ROBERTSON and H. K. BIRNBAUM, *Acta Metall.* **36** (1988) 2193.
6. I. O. SHIM and J. G. BYRNE, *Mater. Sci. Engng A* **123** (1990) 169.
7. B. CRAIG, "Metals handbook, Vol. 13, Corrosion", 9th Edn (ASM, Metals Park, OH, 1987) p. 145.
8. J. EASTMAN, F. HEABAUM, T. MASTSUMOTO and H. K. BIRNBAUM, *Acta Metall.* **30** (1982) 1579.
9. J. CRANK, "The mathematics of diffusion", 2nd Edn (Clarendon Press, Oxford, 1975), p. 48.
10. D. W. DeWULF and A. J. BARD, *J. Electrochem. Soc.* **132** (1985) 2965.

Received 4 September 1992  
and accepted 11 January 1993