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* Corresponding author
E-mail address: stan_kut@prz.edu.pl
(Dr inż. Stanisław Kut)

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Hardness Variations on a Hydrogenated Tin Brass Heat Exchanger

Amjad Saleh El-Amoush [a]*

[a] Al-Balqa Applied University, College of Engineering, Materials and Metallurgical Eng Al-Salt 19117

KEY WORDS
Tin brass Heat Exchanger, Microhardness, Hydrogen

ABSTRACT
Tin brass heat exchanger tube was hydrogen charged under different cathodic charging conditions. The introduction of charged hydrogen into tin brass tube was found to induce hardening on its surface. The severity and the depth of the hardened region was observed to increase with either cathodic current density or charging time. Ageing after charging results in either complete or partial recovery of hardness, depending on the charging conditions applied to heat exchanger tube.

1. Introduction

The effect of hydrogen on hardness of the metallic materials has been reported by several investigators. A. Lost and J.B. 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 γ -lattice. A. Lost et al [1] found 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 γ-lattice. Panagopoulos and Papapanayiotou [2] found that cathodic hydrogen charging of Al-4Zn^{-1}Mg alloy produced major surface hardening and that the microhardness increased with both the charging current density (c.d.) and charging time. Their observations have been explained in terms of the dislocation pinning mechanism. They also found that the microhardness of 'hydrogen-charged Al-4Zn-1Mg decreased during natural ageing and that the surface layer did not recover its original hardness with passage of time after charging. Watson et al [3] found that hydrogen increased the mobility of the dislocation in aluminum alloy. When the charging of hydrogen was stopped, the dislocation behavior reverted to that prior to the charging 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. Matsui et al observed that hydrogen-induced softening at temperature between 190 and 300 K and is caused by the enhanced mobility of screw dislocations due to 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 considered to be due to the interaction of hydrogen clusters with the edge component of dislocations [9].

Hirth [11] found that if the concentration of hydrogen is insufficient, clusters are not formed and therefore there is no hardening; softening occurs instead. Cathodic charging of hydrogen has been observed to produce dislocations near the charging surface

in titanium-molybdenum alloys. It was concluded that the dislocations were created due to hydrogen concentration gradient between the charging surface and the sample bulk.

The objective of this work was to determine the effect of cathodic hydrogen charging on microhardness of tin brass heat exchanger tube. An attempt has been made to determine the penetration depth of cathodically charged hydrogen into the tin brass specimens using microhardness measurements across the thickness of the tube.

2. Experimental Procedure

The material used in this investigation was tin brass heat exchanger tube with diameter of 20mm and 2mm in thickness. The material was supplied by the Jordan Petroleum Refinery Company. The chemical composition and mechanical properties of this alloy are listed in Table 1 and Table 2 respectively. A number of specimens (10 mm wide rings) were cut from this tube. 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 by machining. Prior to cathodic charging, oxide scale formed during annealing was removed by abrading in 600-grit emery paper, then electrolytically polishing and finally pickling in a solution of 5 parts nitric acid, 5 parts orthophosphoric and 1 part acetic acid.

Table 1: *Chemical Composition (in wt%) of Tin Brass Heat Exchanger Tube.*

Cu	Zn	Fe	Si	Sn	Pb
71.72	26.88	0.12	0.04	1.18	0.06

Table 2: *Mechanical Properties of Tin Brass Heat Exchanger Tube.*

Ultimate Tensile Strength, MPa	Yield Strength, MPa	Hardness, $Kg.mm^{-2}$	Elongation, %
365	152	95	65

Electrolytic polishing technique used a two electrode cell comprising of a stainless steel as cathode and sample as anode. The electrolytic solution contained 40 vol.% orthophosphoric and 60vol.% water at room temperature. Constant cell voltage of 1.5V was applied to the specimens. These conditions invariably produced re-producible results. The equipment for electrolytic polishing is consisted of electrolytic cell in which the cathode and anode are suspended in a glass vessel and connected to power supply with direct current. Magnetic stirring is used to the electrolytic solution.

The cathodic hydrogen charging technique used a two electrode cell comprising of a graphite electrode as anode and sample as cathode. The electrolytic solution contained 75% (volume) methanol, 22.4% (volume) distilled water, 2.6% (volume) sulphuric acid and $10mg.l^{-1}$ arsenic trioxide to inhibit hydrogen recombination at the surface.

Constant current densities between 5 and 85 mA.cm-2 were applied to the specimens. The hydrogen charging time varied from 5 hours up to 72hours. The charging of hydrogen into these specimens was provided from the inner surface of the tube specimens. The experiments were performed at room temperature.

The microhardness was measured immediately after cathodic hydrogen charging and after various time intervals. Microhardness was measured across the thickness (perpendicular to tubing axis) in three distinct areas; (A) near-charged, (B) interior and (C) near-outer surfaces of the tube. The width of each area across the tube thickness is shown in Fig. 1. Indentation measurements were carried out with a Vickers indenter at 25g load for 20 seconds. Each reported value is an average of three measurements.

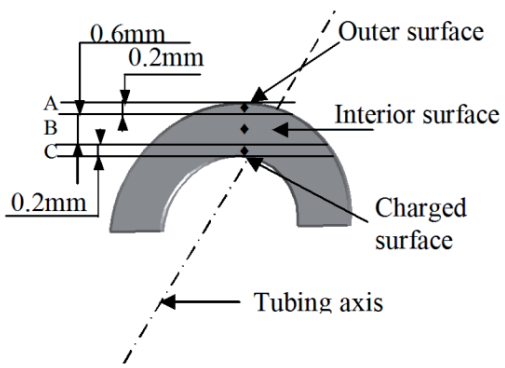

Fig. 1: *Schematic diagram of the specimen section used for measuring the microhardness at different areas across the thickness of specimen (perpendicular to tubing axis, (A) near-charged, (B) interior and (C) near-outer surfaces.*

3. Results and Discussion

3.1 Surface Microhardness Measurements

Microhardness measurements revealed that cathodic hydrogen charging caused hardening on

the surface of tin brass 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 may be attributed to solute hydrogen and dislocation pinning at the surface region. Solute hydrogen atoms acts as dislocation pinning sites contributing to the work hardening of the alloy [2]. The observed increase in microhardness can be explained by decreasing the dislocation mobility resulted from charged hydrogen. It seems 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 after 5 hours of hydrogen charging of tin brass is shown in Fig. 2, which revealed that the hardness increased rapidly after charging at approximately 15mA.cm^{-2}. However, cathodic charging at c.d. lower than 15mA.cm^{-2} did not noticeably affect the hardness of the materials. This may be attributed to the insufficient hydrogen concentration trapped in the materials at lower c.d. The percentage increase of microhardness as a function of cathodic current density (charging time was 5 hours) is calculated referring to the uncharged specimen. The results of this semiquantitative study of the percentage increase in microhardness are shown in Fig. 3. As can be seen from this figure the maximum percentage increase of microhardness Δ (MH)ICD is 64 %.

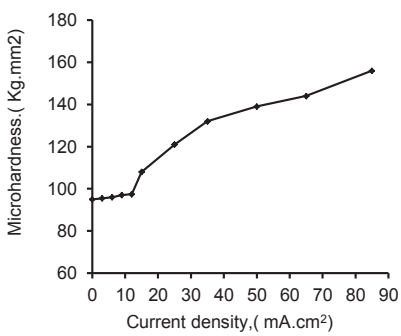

Fig. 2: *Effect of current density on surface Vickers microhardness of tin brass (for charging time of 5 hours).*

The effect of the charging time on surface microhardness of tin brass is shown in Fig. 4, which revealed that the hardness increased rapidly only after 10 hours of charging. However, cathodic charging for shorter time than 10 hours did not affect the hardness much. This may be attributed to the insufficient hydrogen concentration trapped in the materials at shorter charging time. The percentage increase in microhardness as a function of hydrogen charging time at c.d. of 5 mA.cm^{-2} is shown in Fig. 5. As can be seen from this figure, the maximum percentage increase in microhardness Δ(MH) t_{CH} is 80%. Thus the Δ(MH)t_{CH} is higher than Δ(MH) ICD, This reveals that cathodic hydrogen charging for longer times (at c.d. of 5 mA.cm^{-2}) produced a relatively more hardened surface region than that at higher c.d. (with charging time of 5 hours). This observation may due to the different saturating hydrogen contents of the surface region achieved by the two previous cathodic charging conditions, since the surface region is more quickly saturated with hydrogen during the cathodic charging at higher c.d. than those of long-time of charging.

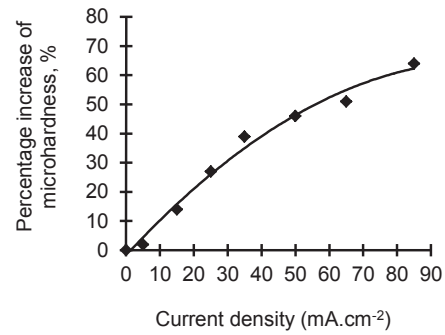

Fig. 3: *Percentage increase of surface Vickers microhardness of tin brass as a function of current density (for charging time of 5 hours).*

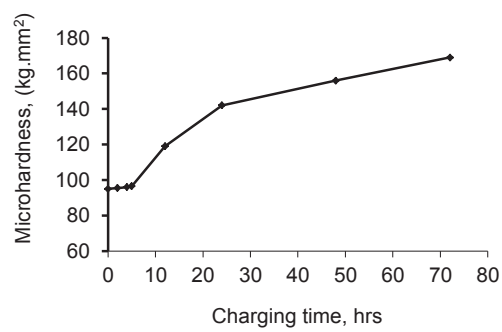

Fig. 4: *Effect of charging time on surface Vickers microhardness of tin brass (for c.d. of 5mA.cm^{-2}).*

3.2 Depth of Hardening

Additional microhardness measurements were made across the thickness (perpendicular to tubing axis) 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 and near-outer surfaces as compared to the uncharged specimen. The near-charged, the interior and near-outer surfaces are indicated by A, B and C respectively. The severity of microhardness on these areas as a function of c.d. and charging time are shown in Figs. 6 and 7 respectively. It is clear that the microhardness increases with increasing charging time and c.d.

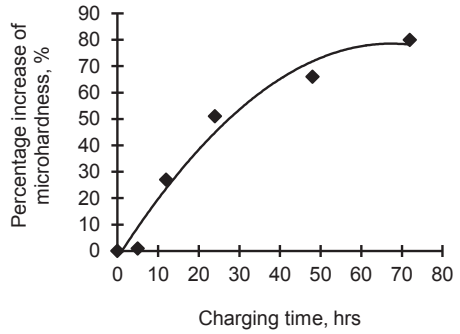

Fig. 5: *Percentage increase of microhardness of tin brass as a function of charging time (for c.d. of 5mA.cm^{-2}).*

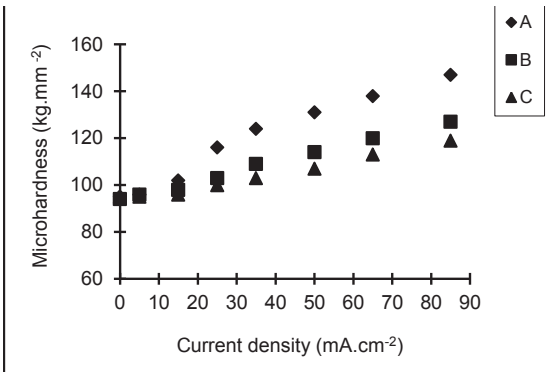

Fig. 6: *Effect of current density on the severity of microhardness across the thickness of tin brass specimens; (A) near-charged, (B) interior and (C) near-outer surfaces (for charging time of 5 hours).*

It is also evident that the depth of the hardened region increases with the cathodic c.d. and charging time. The effect of the cathodic c.d. on the depth of hardening across the thickness of the tin brass specimens is shown in Fig. 8. Based on the results shown in this figure, charging (for 5 hours) at cathodic c.d. of 15mA.cm^{-2} did not affect the hardness of the near-charged surface of the specimen which, indicated that hydrogen did not diffuse to the near-charged surface during this cathodic charging condition. However a cathodic charging condition of 25mA.cm^{-2} current density was found to increase the hardness of the near–charged and interior surfaces, while the hardness of the near-outer surface was not affected. This result showed that the near-charged surface was saturated during the cathodic charging condition of 25mA.cm^{-2} c.d. The further increase in the current density resulted in an increase in the depth of the hardened surface region as shown in Fig. 8. Furthermore, the results confirmed that the long-time charging causes hydrogen to diffuse into the specimen, while the diffusion of hydrogen during the charging at higher current densities might be limited to the surface region.

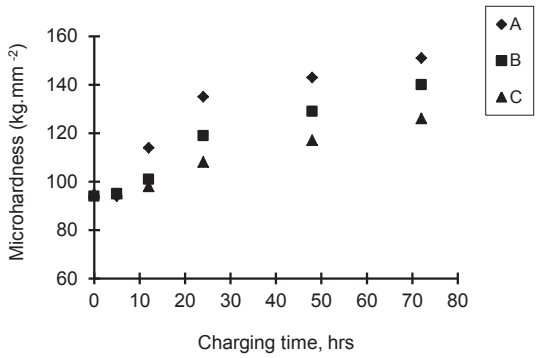

Fig. 7: *Effect of charging time for a constant current density of 5mA.cm-2 on the severity of microhardness across the thickness of specimen; (A) near-charged (B) interior and (C) near-outer surfaces (for c.d. of 5mA.cm^{-2}).*

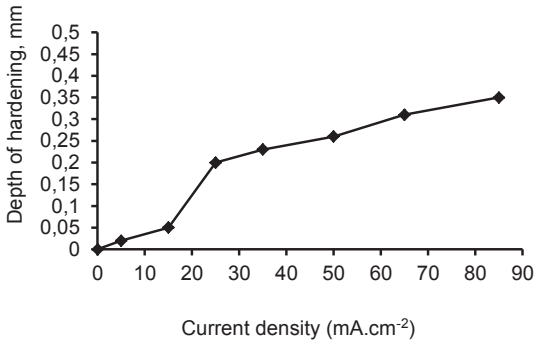

Fig. 8: *Effect of cathodic current density on the depth of hardening of tin brass specimens (for charging time of 5 hours).*

The effect of the charging time on the depth of hardening across the specimen thickness was also examined. Microhardness measurements, which were conducted on the near-charged surface layer of the specimen charged for 12 hours (the current density was maintained at a constant value of 5mA. cm^{-2}) revealed a slight hardening in this region. However, the hardness of the interior and near-outer surfaces was not affect by this cathodic charging condition. Consequently, cathodic charging for 24 hours resulted in an increase of hardness of the near-charged surface while the hardness of interior and near-outer surfaces is slightly increased. These results confirmed that the microhardness is increasing steadily in near-charged, interior and near-outer surfaces after 24 hours charging. The trend continues even after 40 hours of charging. However, further charging beyond 40 hours appears to increase the depth of the hardened surface region as shown in Fig. 9.

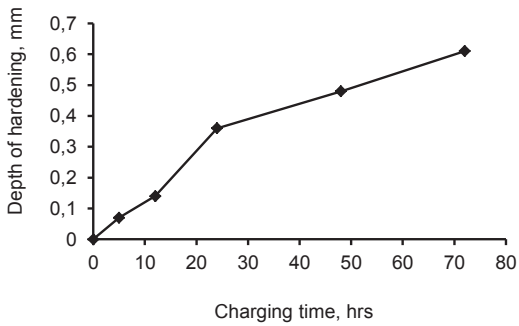

Fig. 9: *: Effect of charging time on the depth of hardening of tin brass specimens (for c.d. of 5mA.cm^{-2}).*

It was noted that further cathodic charging and further increase in the current density appear to increase the microhardness of the external and the interior surfaces of tin brass specimens. The hardening induced by charged hydrogen into the investigated material is due to decreased dislocation mobility and increased dislocation density.

Hydrogen was observed to increase the mobility of the dislocation in aluminum alloy [12]. However, 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 [5,6] and iron [7,13] 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 [14].

It was found that below a temperature of 190 K and typically around 170 K, hydrogen causes softening in iron when 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 [13].

Hirth [11] found that if concentration of hydrogen was insufficient, the clusters were not formed and hence it did not cause hardening, but caused softening instead. The present experiments clearly demonstrate a macroscopic hardening of tin brass heat exchanger tube charged cathodically at higher current densities and longer charging times. However, no softening was observed even at lower c.d. or shorter charging times.

3.3 Recovery of hardness during ageing

It is well recognized that hydrogen increases in concentration within voids or fissures, creating a large internal pressure which enhances void growth and crack propagation [15, 16]. The diffusion of hydrogen is fairly fast even at room temperature (The diffusion coefficient of hydrogen in brass at 25°C ~ 10-9$cm^2.s^{-1}$ [17]), the desorption of hydrogen from metals takes a much longer time than its absorption because of the trapping of hydrogen in these structural imperfections. Therefore, microhardness was measured at certain time intervals after charging to assess the reversibility of the hardening on account of the desorption of hydrogen.

Figure 10 shows effect of ageing time and current density on loss of microhardness. It is evident that the microhardness decreases with increasing ageing time. It is also evident that specimens charged at higher current densities (higher than 25 mA.cm^{-2}) do not soften up to original hardness even after 120 minutes. It means it will require longer ageing time. Those charged at lower c.d. have recovered original microhardness fully. Figure 11 shows effect of ageing time and charging time on loss of microhardness. It is evident that microhardness decreases with increasing ageing time. It is also evident that specimen charged for longer duration (longer than 12 hours) do not fully soften up to original micro-

hardness. Those charged for 12 hours or less have recovered original microhardness fully.

It was observed that the microhardness of the specimens charged for longer charging time took longer ageing time to decrease than those charged at higher c.d. As shown in Fig. 11, 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 only 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 those charged at higher c.d. This is attributed 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.

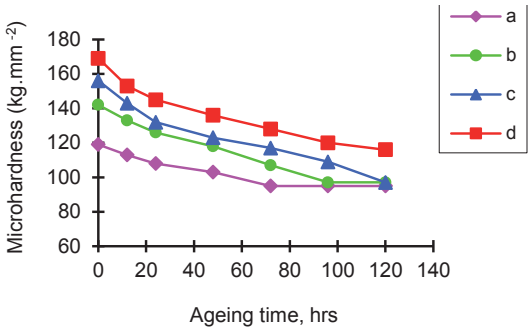

Fig. 10: *Effect of ageing time and current density on loss of microhardness -(a) 15mA.cm^{-2}, (b) 25mA.cm^{-2}, (c) 35mA.cm^{-2}, (d) 50mA.cm^{-2}, (e) 65mA.cm^{-2}, (f) 85mA.cm^{-2}, current densities (for charging time of 5 hours).*

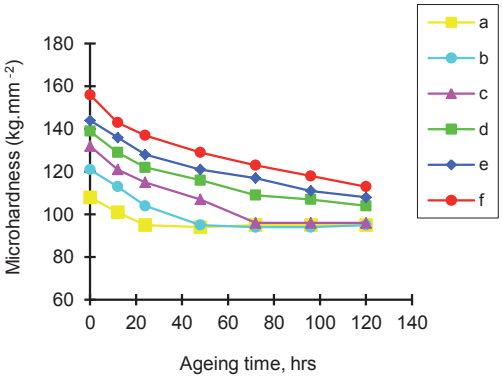

Fig. 11: *Effect of ageing time and charging time on loss of microhardness -(a) 12 hrs, (b) 24 hrs, (c) 48 hrs, (d) 72 hrs. (for c.d. of 5mA.cm^{-2}).*

4. Conclusion

1. Microhardness of tin brass is increased considerably by cathodic hydrogen charging. The increase in microhardness depends on both c.d. and charging time. The microhardness of tin brass is not affected by cathodic charging at lower c.d. or lower charging times.

2. A more severely hardened surface region is observed in the specimen charged for longer times than those charged at higher c.d.

3. The depth of the hardened region is increased by both the cathodic c.d. and charging time. However, the depth of hardening of the specimens charged for longer times than those charged at higher c.d.

4. During natural ageing, hardness is recovered fully or partially, depending on the cathodic hydrogen charging applied to the tin brass specimens. The specimens charged at higher current density and those for longer time of charging are fully recovered to the original microhardness during natural ageing. However, the specimens charged at lower current density and those for shorter charging time are showed completely reversible behavior after the above period of natural ageing. It is observed that the microhardness of the specimens charged for longer charging time took longer time of ageing to decrease more than those charged at higher current density.

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