



## Short Communication

## Why copper may be able to corrode in pure water



G. Hultquist

Surface and Corrosion Science, Royal Institute of Technology, SE-100 44 Stockholm, Sweden

## ARTICLE INFO

## Article history:

Received 26 July 2014

Accepted 1 January 2015

Available online 7 January 2015

## Keywords:

A. Copper

C. Hydrogen absorption

C. Oxidation

## ABSTRACT

In exposure of copper to water molecules there will be relatively strong bonds (reversible traps) between copper and hydrogen. One copper–hydrogen bond corresponds to the thermal energy of a temperature of approximately 250 °C and this explains an unusual temperature influence on hydrogen uptake in the metal and in corrosion of copper in pure water–vapour without O<sub>2</sub>. This unusual temperature influence is exemplified in exposure of copper at 180 °C and 500 °C where Cu corrodes more at 180 °C than at 500 °C.

© 2015 Elsevier Ltd. All rights reserved.

## 1. Introduction

It was observed almost 30 years ago that copper released hydrogen to the gas phase when immersed in pure liquid water [1]. This was unexpected and was questioned in several papers mainly based on thermodynamic arguments but without consideration of any copper–hydrogen bonds [2,3]. Since water molecules are made up from both oxygen and hydrogen a relevant knowledge of the copper–hydrogen bonds is necessary to be included in the judgment of stability of copper in water. This means that both copper–hydrogen bonds as well as the bonds of O-containing species should be known before comparison with the stability of the water molecule can be made. This approach was taken in a fundamental paper on the interaction of water with solid surfaces by Thiel and Madey [4]. Recently, the amount of hydrogen in copper and other metals has been measured with thermal desorption spectroscopy (TDS) after more than 10 years exposure in ambient air [5]. The results show that all the analysed metals except gold contained hydrogen to a measurable amount.

This short communication presents results from the TDS-method used in [5] after exposure of copper to water vapour without O<sub>2</sub> at 120 °C, 180 °C and 500 °C. These temperatures are below and above 250 °C, the temperature where most hydrogen is outgassed from copper and thereby below and above the energy of a main copper–hydrogen bond. With this choice of temperatures we can examine a possible influence of hydrogen-uptake in copper on the corrosion of copper in water vapour without molecular oxygen.

## 2. Experimental

The studied oxygen free phosphorous copper (OFP-copper) was 99.99% Cu with 57–70 ppm phosphorous deliberately added for mechanical reasons. This copper was obtained from the Swedish Radiation Safety Authority. After cutting, sample dimensions were 5.5 mm × 5.5 mm × 18 mm, dry polished (no liquids) down to 2400 mesh with SiC-paper. The TDS-method was stepwise with an increase of temperature every 12 h except for 20 h at 20 °C. In contrast to a continuous increase of temperature in a ramp, the diffusion can be more easily seen in the used TDS-method. Also a slow temperature increase is favourable for identification of the temperature influence on traps. Additional details of the TDS method may be found in Ref. [5]. The water–vapour was prepared by opening of approximately 1 cm<sup>3</sup> liquid water to an evacuated volume ≈1500 cm<sup>3</sup>. This evacuation and opening was repeated several times in order to remove any residual air in the gas-phase and in the liquid water. The partial pressure of O<sub>2</sub> should then be <2 × 10<sup>−4</sup> mbar. The amount of H<sub>2</sub> was calculated from a known pressure of H<sub>2</sub> in a known volume. Quantification of water in Table 1 (below) was done by using the nominal sensitivity ratio in the mass spectrometer between water and H<sub>2</sub>. A careful outgassing of the quartz-tube and the Ti-element in the ion-pump preceded the experiment with the Cu-sample. After TDS up to 600 °C the sample contained ≤0.02 wt ppm hydrogen. Data in the figures are after subtraction of data from blank (without Cu) experiments and exposures.

## 3. Results and discussion

After dry polishing and exposure (storage) for 120 h in ambient air the sample contained 0.51 wt ppm hydrogen which is a typical

E-mail address: [gunnarh@kth.se](mailto:gunnarh@kth.se)

value for Cu [5]. (The details of the production of the copper are not known but as a last step the polished sample was exposed to ambient air for 120 h.)

Figs. 1 and 2 show hydrogen outgassing from the TDS-measurements. In Fig. 2, a main increase at 250 °C in the temperature distribution (fraction) of outgassing is more clearly seen. This phenomenon is interpreted as being due to a main Cu–hydrogen bond at approximately 250 °C. However, some hydrogen is also out-gassed at higher temperatures. The presence of intrinsic vacancies, which for energetic reasons, can be emptied (outgassed) of hydrogen, can be a reason for the observed peak. After this outgassing in the TDS-measurements the sample is judged to contain  $\leq 0.02$  wt ppm hydrogen. With this low hydrogen content, the sample was exposed to water-vapour at 180 °C. The exposure at 500 °C of the same sample was also preceded by TDS and therefore the sample also contained  $\leq 0.02$  wt ppm hydrogen at the start of this exposure.

Fig. 3 shows a difference in outgassing of H<sub>2</sub>O in TDS between the exposure in the water-vapour without molecular oxygen (O<sub>2</sub>) for 120 h at 180 °C and 500 °C. Fig. 4 shows a corresponding difference in hydrogen at the two temperatures.

The difference in the temperature distribution of hydrogen in the exposure at the two temperatures is even more clearly seen in Fig. 5. The temperature obviously had a major influence on the

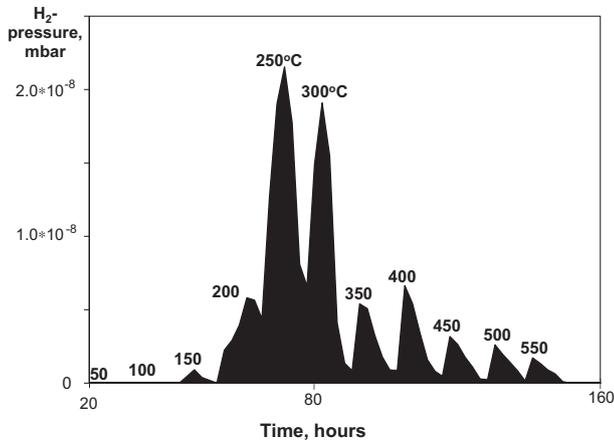


Fig. 1. Outgassed H<sub>2</sub> from as received 2500 mesh dry mech. pol. Cu-sample followed by 120 h in ambient air. Black area corresponds to the amount of hydrogen.

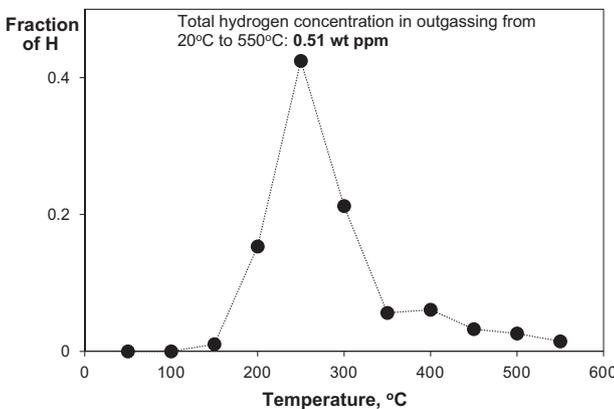


Fig. 2. Fraction of outgassed hydrogen at different temperatures from as received 2500 mesh dry mech. pol. Cu-sample followed by 120 h in ambient air. Data obtained from Fig. 1. (The content corresponds to unity of fraction.)

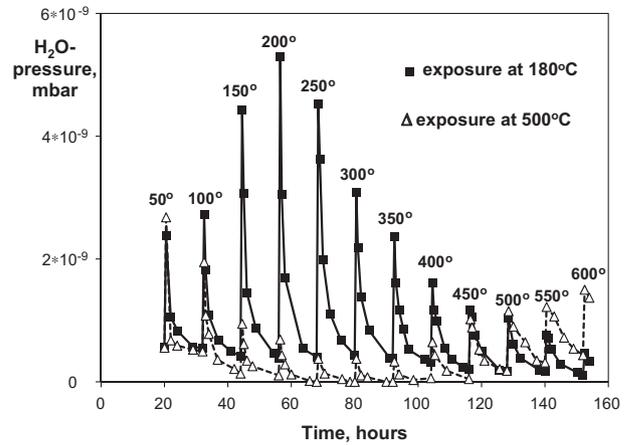


Fig. 3. Outgassed H<sub>2</sub>O from 120 h exposed Cu-sample in 10 mbar H<sub>2</sub>O at 180 °C and 500 °C respectively. Area under respective curve gives water content.

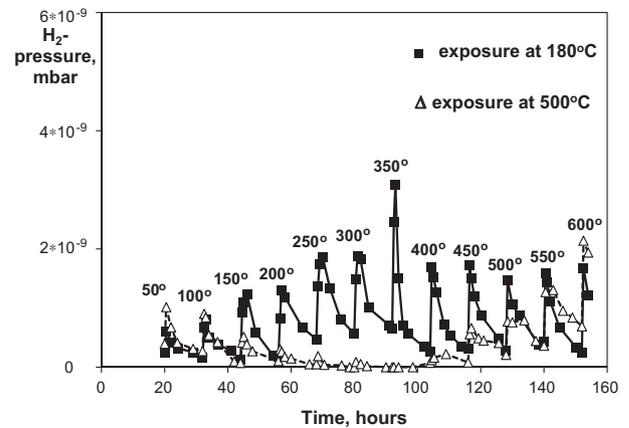


Fig. 4. Outgassed hydrogen from 120 h exposed Cu-sample in 10 mbar H<sub>2</sub>O at 180 °C and 500 °C respectively. Area under respective curve gives hydrogen content.

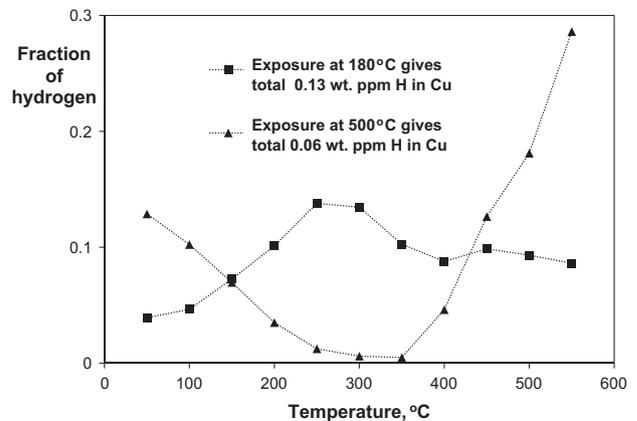
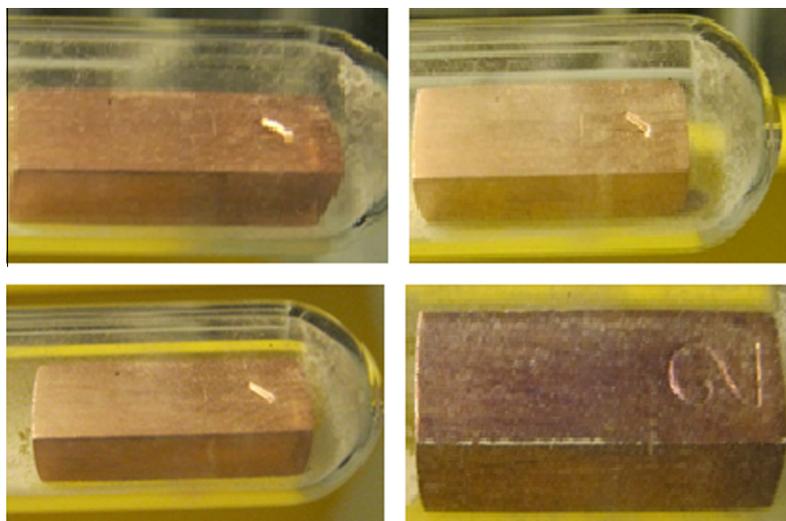


Fig. 5. Fraction of outgassed hydrogen at different temperatures after exposure in 10 mbar H<sub>2</sub>O for 120 h at 180 °C and 500 °C. Before exposures  $< 0.02$  wt ppm H, 0.13 wt ppm H after exposure at 180 °C and 0.06 wt ppm H after exposure at 500 °C. (The contents correspond to unity of fraction.)

total hydrogen uptake during the exposures as well as its distribution. The distribution is in accordance with a main Cu–hydrogen bond near 250 °C present in Fig. 2 where the Cu-sample was exposed to ambient air for 120 h.



**Fig. 6.** Visual appearance after various exposures. Upper left, after 120 h in 10 mbar H<sub>2</sub>O without O<sub>2</sub> at 180 °C. Upper right, after 120 h in 10 mbar H<sub>2</sub>O without O<sub>2</sub> at 180 °C plus TDS at 50–550 °C. Lower left after 120 h in 10 mbar H<sub>2</sub>O without O<sub>2</sub> at 500 °C. Lower right after 288 h in 10 mbar H<sub>2</sub>O without O<sub>2</sub> at 180 °C followed by 400 h in 10 mbar H<sub>2</sub>O without O<sub>2</sub> at 120 °C.

**Table 1**

Hydrogen (H) and water in TDS from various exposures of 4.7 g Cu with dimensions 5.5 mm × 5.5 mm × 18 mm. Data based on outgassing in the 20–550 °C temperature range.

Exposure	H (μmole)	H <sub>2</sub> O (μmole)
Ambient air, 30–40% relative humidity, 120 h, 20 °C	2.37 <sup>a</sup>	0.26 <sup>a</sup>
10 mbar H <sub>2</sub> O, 120 h, 180 °C	0.60	0.64
10 mbar H <sub>2</sub> O, (288 h, 180 °C) + (400 h, 120 °C)	1.48	0.78
10 mbar H <sub>2</sub> O, 120 h, 500 °C	0.26	0.30

<sup>a</sup> Unknown history of bulk of Cu before exposure for 120 h in ambient air.

Since both H<sub>2</sub>O and H<sub>2</sub> are emitted in the outgassing and any other O-containing species like CO, CO<sub>2</sub> and O<sub>2</sub> were negligible, the only emitted species with O in the out-gassing was H<sub>2</sub>O after the water-vapour exposures. Therefore it can be concluded that O is taken up not only in the surface but also in the bulk of the Cu-sample in the exposures where uptake in the bulk equals half the amount (in moles) of outgassed hydrogen (H) in the TDS. Consequently, it must be expected that 1–2 wt ppm O is taken up in the bulk due to the water-vapour exposure for 120 h at 180 °C. This uptake was confirmed in an analysis (by a commercial company) where the sample oxide was removed and the sample was melted in the subsequent analysis. This uptake of O in the bulk of Cu will not contribute to the surface appearance of the Cu-sample.

The difference in appearance of the Cu-sample before and after exposures is seen in Fig. 6. This figure shows that exposure to water-vapour produces a solid reaction product. A thickness of the over-layer on the surface of the sample can be judged to be a few hundreds of Angstroms from the tarnish in Fig. 6. Since not all of the outgassed hydrogen and water come from the macroscopic surface area, the data in Table 1 are not normalised to the macroscopic surface area of the sample (4.5 cm<sup>2</sup>). Included in this table are data from a longer exposure time of 288 h at 180 °C plus 400 h at 120 °C with a measured higher outgassed amount of both H<sub>2</sub> and H<sub>2</sub>O. This longer exposure results in a more noticeable tarnished film in Fig. 6 (lower right).

The solid reaction product causing the tarnished film in Fig. 6 is produced from the dissociation of water-molecules. Both in Table 1

and in the visual appearance of the surfaces in Fig. 6 is seen the unusual temperature influence upon exposure at <250 °C compared to 500 °C in oxygen-free water-vapour. Copper corrodes less at 500 °C compared to 180 °C. This phenomenon is also observed when using the 99.95+%, 0.1 mm thick Cu-sheets from [6]. It can be noted that hydrogen is taken up to a lesser extent in a single-crystal of Cu [5] compared with the polycrystalline Cu-sample used in this study.

#### 4. Conclusions

1. A main bond between copper and hydrogen is over-come by the thermal energy associated with temperatures >250 °C.
2. Copper corrodes less in O<sub>2</sub>-free water vapour upon exposure at 500 °C compared with exposure at 180 °C.
3. Exposure at 180 °C for 120 h to 10 mbar water-vapour without O<sub>2</sub> gives a visible solid reaction product and an uptake of oxygen in the metal.

#### Acknowledgements

M. Graham and J. Smialek are gratefully acknowledged for valuable comments. The Swedish Radiation Safety Authority is also gratefully acknowledged for financial support.

#### References

- [1] G. Hultquist, Hydrogen evolution in corrosion of copper, *Corros. Sci.* 26 (1986) 173–176.
- [2] T.E. Erikson, P. Ndalamba, I. Grenthe, On the corrosion of copper in pure water, *Corros. Sci.* 29 (1989) 1241–1250.
- [3] J.P. Simpson, R. Schenk, Hydrogen evolution from corrosion of pure copper, *Corros. Sci.* 27 (1987) 1365–1370.
- [4] P. Thiel, T. Madey, The interaction of water with solid surfaces, *Surf. Sci.* 7 (1987) 211–385 (Reports rev. article 7).
- [5] G. Hultquist, M.J. Graham, J. Smialek, B. Jönsson, Hydrogen in metals studied by thermal desorption spectroscopy (TDS), *Corros. Sci.*, accepted for publication.
- [6] G. Hultquist, M.J. Graham, O. Kodra, S. Moisa, R. Liu, U. Bexell, J.L. Smialek, Corrosion of copper in distilled water without O<sub>2</sub> and the detection of produced hydrogen, *Corros. Sci.*, submitted for publication.