# Corrosion of copper in distilled water without O₂ and the detection of produced hydrogen

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A B S T R A C T

This paper reports on hydrogen pressures measured during ~19,000 h immersion of copper in oxygen-free liquid distilled water. Copper corrosion products have been examined *ex-situ* by SEM and characterized by XPS and SIMS. XPS strongly indicates a corrosion product containing both oxygen and hydrogen. SIMS shows that oxygen is mainly present in the outer 0.3 µm surface region and that hydrogen penetrates to depths well below the corrosion product. Thermal desorption spectroscopy shows that the reaction product formed near room-temperature is less stable than that formed in air at 350 °C.

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## 1. Introduction

Release of hydrogen upon immersion of a metal in liquid water is evidence for reaction between the metal and the water [1]. A summary of ultrahigh vacuum (UHV) experiments and considerations of stabilities of various products in metal–water reactions has been presented in [2]. However, a printing error in [2] ($-30$ should be $+30$ kJ mole$^{-1}$) concerning the stability of a hydrogen-free reaction product means that a hydrogen-containing reaction product (CuOH) is favoured over a hydrogen-free reaction product (CuO and Cu$_2$O) in the Cu–water reaction. This fact is not generally known and emphasizes the need for characterization of hydrogen in the reaction product.

The first report of hydrogen gas evolution from Cu-corrosion at room temperature in liquid distilled water in the absence of any applied potential and in the absence of O$_2$ was made almost 30 years ago [3]. This has been followed by relatively recent work [4–6]. The measured hydrogen gas pressure will ultimately be in the mbar ($10^2$ N m$^{-2}$) range. This pressure is of the order of a thousand times higher than the hydrogen gas pressure in ambient air [7].

It has been argued, however, that this detection of H$_2$ must be the result of something other than reaction of Cu with water.

These arguments are mainly based on that the second law of thermodynamics is violated and consequently other reactions than copper corrosion have been suggested [8,9]. Due to the importance of the application of final storage of nuclear waste in Cu-canisters, a serious attempt was recently made to repeat the experiments in [4,5]. Results confirming the detection of hydrogen gas are reported in [10]. These previous experiments were performed with copper contained in leached glass within a 316 stainless steel system. Here we also report hydrogen gas measurements where the stainless steel container is replaced by titanium to exclude that the measured hydrogen originates from the container material as was suggested in [9].

Previously [4,5], it was found that the formed product contains hydrogen and in this work we also present *ex-situ* characterization of the reaction product in O$_2$-free liquid water and O$_2$-free water-vapor. The products formed in liquid water are from an approximately total two years exposure (19,000 h) of Cu in distilled water in the 21–55 °C temperature range. The *ex-situ* characterization is performed by field emission gun scanning electron microscopy (FEG-SEM), X-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS) and thermal desorption spectroscopy (TDS). TDS-data from outgassing of copper after exposure in water-vapor at 350 °C is also presented.

Finally a model is presented for the corrosion of copper in oxygen-free water which summarizes some factors overlooked in a

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prediction based on traditional thermodynamics of copper in water.

## 2. Experimental

The ultra-high vacuum (UHV) experimental setup has been described in detail in previous publications [4,5]. Briefly, hydrogen gas pressures are measured with an absolute pressure meter and a mass spectrometer is employed for verification of the hydrogen gas. An example of a mass spectrum is shown in [5] where also a schematic of the equipment is found. All experiments are with a palladium membrane of a thickness 0.1–0.2 mm through which only hydrogen will be transported. The fastening of the palladium membrane is crucial for the measurements of hydrogen. It is essential to apply the right pressure in forcing the edge of stainless steel into the thin membrane. An initial evacuation of the compartment placed on one side of the membrane will enable the detection of hydrogen gas with the absolute pressure meter. This evacuation must be thorough and made with a UHV pump for at least 24 h near room temperature. The other side of the membrane is in direct contact with the volume where hydrogen gas is generated during corrosion. Also this volume was evacuated to obtain $O_2$-free conditions as described earlier in detail [5]. Any possible residual $O_2$ after the evacuation is consumed in the early stage of corrosion in the closed system. The UHV system is air-tight and no leaks are detected during the experiments. Before any exposure of copper in glass vessels placed in stainless steel or titanium below the palladium membrane, these containers were filled with boiling distilled water to remove any easily dissolved surface debris. Also the glass was "leached" in boiling water before the copper immersion. Depending on the detection limit of the pressure meter, $H_2$ can be measured down to $\sim 2 \times 10^{-7}$ bar.

Copper of purity 99.95+ wt.%, 0.1 mm thick rolled sheet supplied by Goodfellow was used in the "as received" condition. A typical impurity analysis in ppm is: Ag, 100; As, 200; Cr, 50; Fe, 5; Pb, 2; B, Bi, Mg, Mn and Si, <1. The grain size was $\sim 20\ \mu m$. This copper was used in all exposures except for some in Figs. 9a and 9b where a 2 mm thick Cu-sample (part of UHV-copper gasket in the as received condition) was used.

Analysis of the previously exposed Cu-sheets was performed with FEG-SEM, XPS and SIMS. In the FEG-SEM micrographs an accelerating voltage of 20 kV was used. XPS-analysis was performed in a PHI 5500 spectrometer with a monochromated Al $K_\alpha$ source, SIMS in an PHI Adept 1010 with a primary 4 keV Cs ion beam, and secondary ions from approximately $0.1 \times 0.1$ mm were detected (in Ottawa) and in a Cameca spectrometer with a primary 10 keV Cs source with detected secondary ions from 30 µm diameter and raster area of 200 µm × 200 µm (in Singapore).

Thermal desorption spectroscopy (TDS) was used to assess outgassing after different exposures of Cu, including the $\sim 19,000$ h exposed Cu. This characterization was preceded by a thorough evacuation of a quartz tube (background) up to 900 °C. The sample was inserted and this was followed by an initial evacuation with a turbo molecular pump at room-temperature. Measurements were taken with a mass spectrometer pumped with an ion-pump. The pump-element of titanium was outgassed in a separate ion pump to remove hydrogen in order to obtain a low detection limit for hydrogen. In TDS the sample temperature was increased 50 °C in a stepwise fashion every 12 h.

## 3. Results and discussion

### 3.1. Detection and measurement of $H_2$

Fig. 1 shows detected hydrogen gas pressures during the last 5000 h of the almost 19,000 h exposure of 140 cm$^2$ copper sheets

in 90 ml distilled water in a glass container within a stainless steel vessel. The detected hydrogen gas pressures at shorter exposure times in the same experiment are found in [4,5]. The hydrogen pressure increase due to copper corrosion is clearly observed in Fig. 1, where the same rate of $H_2$-increase due to copper corrosion is pointed out at 14,500 and 17,800 h. It is also seen that temperature increases produce rapid increases in measured hydrogen pressure due to decreases in the amount of hydrogen in the palladium and vice-versa. At 17,000 h there is almost no change of pressure due to a steady state between formation (oxidation) and reduction of the corrosion product. This steady state does not depend on the hydrogen content in the palladium membrane.

It is possible to estimate the corrosion rate from the increase of $H_2$-pressure at a certain temperature in Fig. 1. This estimate is based on the volume where the pressure is measured and the area of Cu exposed. In this estimate we neglect a small part of hydrogen present in the palladium membrane. We find a hydrogen gas production rate of $\sim 4 \times 10^{-10}$ moles per hour both at 14,500 and 17,800 h in Fig. 1. With this measured generation rate of hydrogen, assuming a density of a reaction product of 4 g cm$^{-3}$ and the simplified reaction $Me + H_2O \rightarrow MeO + H_2$ (measured) we can calculate a metal corrosion rate. This means that the assumed simplified reaction product does not contain any hydrogen. This calculation will result in an underestimation of the thickness of the corrosion product, in that hydrogen contained in the corrosion product, in the copper metal and in the palladium membrane is not taken into account. The extent of underestimation depends on the thickness of the corroding sample and the palladium membrane and the true corrosion rate may be at least a factor of three higher than that calculated from hydrogen gas release rates. With this factor taken into account the corrosion rate for the copper sheets is estimated to be 0.01–0.1 µm per year at room temperature.

Fig. 2 shows hydrogen gas measurements of 20 cm$^2$ copper sheets in 15 ml of distilled water in a glass container within a titanium vessel. An almost time independent hydrogen gas pressure in the mbar range ($10^2$ N m$^2$) is also found in the figure and this takes place at $\sim 7800$ h.

A steady-state of hydrogen gas generation (constant measured $H_2$) in Cu-corrosion is clearly not dependent on either stainless steel or titanium as the background (container) material. This is illustrated in Fig. 3 where the same steady state is obtained with these two materials. The experimental data (solid points and one
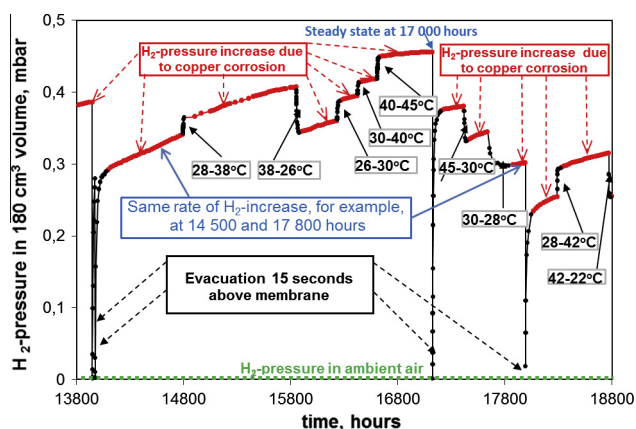


**Fig. 1.** Measured $H_2$-pressure in exposure of 140 cm$^2$ Cu in 90 ml distilled water at 21–26 °C at pH near 7. Evacuation of hydrogen gas above the Pd-membrane and temperature influence of the Pd-membrane in the 22–45 °C range (shown within squared boxes) on measured $H_2$-pressure. Almost no change of pressure at approximately 17,000 h due to a steady state between formation (oxidation) and reduction of a corrosion product. Same rate of increase of $H_2$-pressure indicated at 14,500 and 17,800 h.
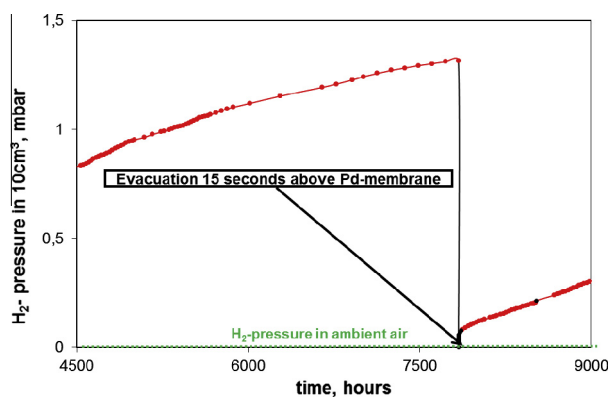
**Fig. 2.** Measurement of $H_2$ during exposure of 20 cm² Cu in 15 ml distilled water at approximately 50 °C. Glass tube placed in a drilled titanium bar with exposed area of 75 cm².

square) in this figure show a steady-state in the 20–55 °C interval which increases with temperature. What does this temperature-dependence reflect? A likely explanation is that increased temperature causes an increased presence of $OH^-$ due to auto-ionization of liquid water. This phenomenon has the same temperature dependence as the experimental change with temperature and therefore most likely shows that the presence (availability) of $OH^-$ rules the steady state. This phenomenon causes increased corrosion at higher temperature and therefore an increased steady state $H_2$-pressure in the 20–55 °C temperature range. However, at temperatures above the temperature range 22–56 °C, the diffusion of hydrogen into the copper sample will increasingly dominate and therefore hardly any increase of hydrogen to the gas phase can be seen with increased temperature [11].

At a steady state there is as a balance between the formation of a reaction product and removal (reduction) of the same reaction product. We consider that this reaction product is CuOH [2,11] and is the first formed reaction product in distilled water. However, this product can transform to $Cu_2O$ with a simultaneous movement of H into a hydrogen trap in the metal.

In air-contact this transformation can also lead to formation of CuO. Under certain conditions no transformation of CuOH may take place. The steady 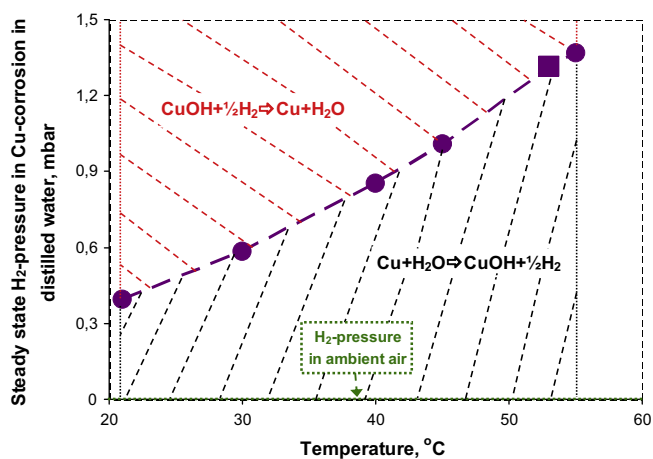state $H_2$ pressure in distilled water increases with temperature: $H_2$ = 0.39 mbar at 21 °C, 0.58 mbar at 30 °C, 0.85 mbar at 40 °C, 1.01 mbar at 45 °C and 1.37 mbar at 55 °C [5]. Therefore temperature has a predictable influence, via the presence of $OH^-$ and $H^+$, on the steady state $H_2$-pressure.

In Fig. 3 at pressures lower than a steady state pressure the reaction product forms:

$$Cu + H_2O \rightarrow CuOH + 1/2H_2 \qquad (1)$$

where a part of the released hydrogen in Eq. (1) can be monitored as $H_2$ in the gas volume above the immersed Cu and another part enters the Cu-metal. It should be noted that the data in Fig. 3 are also supported by results from exposures in water-vapor [11]. In other research it has been shown by TDS that different metals but not gold contain hydrogen after many years in ambient air [12]. In that work it is also shown that the grain size of the Cu-metal is important for the uptake of hydrogen in the metal by performing TDS of a single crystal.

At pressures higher than the steady state pressure the reaction product is reduced back to metallic copper and water:

$$CuOH + 1/2H_2 \rightarrow Cu + H_2O \qquad (2)$$

At a steady state, the rate of formation of a reaction product equals the rate of removal (reduction) of the same reaction product. Upon a temperature decrease at the steady state, e.g. from 55 to 43 °C, a resulting reduction of the reaction product takes place since the concentration of $OH^-$ is lower at the lower temperature.

Several parameters influence the rate of $H_2$ release to the gas-phase where the measurement takes place. Some of these are time of exposure, temperature and $H_2$-pressure. In addition to these parameters the concentration of hydrogen in the Cu-metal will also influence the measured $H_2$-pressure. In Table 1 the rates of measured $H_2$-release at certain times, temperature and $H_2$-pressure in the 18,800 h immersion of Cu are collected and taken from [4,5] and Fig. 1. The $H_2$-release to the gas-phase, reasonably far from a steady state, is expressed as measured increased $H_2$-pressure per hour in the 120 cm³ volume.

From Table 1 we judge the $H_2$-release to the gas-phase increases by approximately a factor 8 when the temperature is increased from 23 to 52 °C. However, as already pointed out the rate at a given temperature can change for many reasons and is therefore hard to predict. On the other hand it is relatively straightforward to calculate the amount of released $H_2$ to the gas phase from [4,5]. We find that the amount of hydrogen released to the gas phase based on measured hydrogen gas pressure, volume and temperature is $\sim$3 × 10$^{-5}$ mole (140 cm² Cu-area) in the 18,800 h exposure. Assuming formation of entirely CuOH with a density of 4 g cm$^{-3}$, this corresponds to a 140 nm thick reaction product.

### 3.2. Characterization of corrosion product

FEG-SEM micrographs are shown in Fig. 4. The left micrograph is of a copper sample which has been stored in ambient air for more than 3 years, whereas the other micrograph is from a sample exposed to $O_2$-free distilled water for 2.2 years followed by a



**Fig. 3.** Steady state $H_2$-pressure vs. temperature in Cu-corrosion in distilled water. Increased temperature causes increased presence of $OH^-$ due to auto-ionization of liquid water and therefore increased steady state $H_2$-pressure. Filled circles from [5] where background material was Stainless Steel 316L and filled square from present work where background material was Ti. Size of marks corresponds approximately to error bar in the measurements.
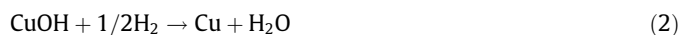
**Table 1**
$H_2$-release to the gas-phase at various time, temperature and $H_2$-pressure.

| $H_2$-release to the gas-phase (mbar, h⁻¹) | Time of exposure (h) | Temperature (°C) | $H_2$-pressure (mbar) |
|---|---|---|---|
| 3 × 10⁻⁴ | 2,900 | 45 | 0.5 |
| 4 × 10⁻⁴ | 5,500 | 52 | 0.7 |
| 0.6 × 10⁻⁴ | 14,300 | 23 | 0.3 |
| 0.5 × 10⁻⁴ | 18,300 | 23 | 0.35 |

6 month exposure to ambient air. In this case a localized corrosion product is clearly seen.

The copper used in the 18,800 h exposure has been analyzed with XPS. Fig. 5 shows the oxygen (O1s) spectrum compensated for charging based on the carbon 1s peak. The spectrum can be fitted to two peaks, but a better fit is obtained for three peaks: 532.0 eV (corresponding to hydroxide [13]), 530.1 eV (corresponding to oxide [13]) and a small peak at 533.5 eV. This last peak at the highest energy could be due to adsorbed water as identified by Grosvenor et al. for iron exposed to water vapor [14]. The Cu 2p (not shown) indicates copper hydroxide at 935 eV [13] but the oxide peaks are overshadowed by the metal peak. The XPS data indicate both copper hydroxide and copper oxide. Typical impurities in the copper were not detected on the surface.

SIMS analysis with ion beam sputtering was performed to examine the corrosion products in-depth and to detect hydrogen. Fig. 6 illustrates dynamic SIMS analysis of oxygen in the outer part of a Cu-sample exposed to air for three years and another to air for one year and liquid water for two years. Clearly this SIMS analysis (performed in Ottawa) shows that the oxide on the water-exposed sample is much thicker than that produced in air. This was confirmed in another SIMS-spectrometer analysis with results shown in Fig. 7. By comparing the depths in Fig. 7 with those in Fig. 8, for the water-exposed sample, hydrogen is found below the oxygen which is mainly on the surface. This seems reasonable since diffusion of hydrogen is higher than for oxygen in most, if not all, materials. An advantage for detection of hydrogen in SIMS is the use of $D_2O$ instead of $H_2O$ due to a lower background of D in the SIMS-spectrometer. However, Cu may not react to the same extent in $D_2O$ mainly because the ion product for $H_2O$ is approximately 10 times higher than for $D_2O$ which means that the availability of $OH^-$ and $H^+$ is higher than that of $OD^-$ and $D^+$ in water [15].

Thermal desorption spectroscopy (TDS) has also been used to characterize the approximately two years ($\sim$19,000 h) exposed Cu in the absence of $O_2$. Results from this analysis are shown in Figs. 9a and 9b. Included in these figures are results from water-vapor and air exposure of Cu. A main result from this characterization is that the reaction product on Cu in exposure to air at 350 °C is different from the reaction product formed in water near room-temperature. Only the Cu-sample exposed at 350 °C remained tarnished after the outgassing indicating formation of a different reaction product than the product formed during exposure at the lower temperatures. Also in this characterization with TDS a considerable amount of hydrogen is outgassed (desorbed) from all samples investigated. Although not shown, a small amount of carbon-containing species were also present in the outgassing after air-exposures, but mainly $H_2$ and $H_2O$ were outgassed after all exposures as detailed in Fig. 9.
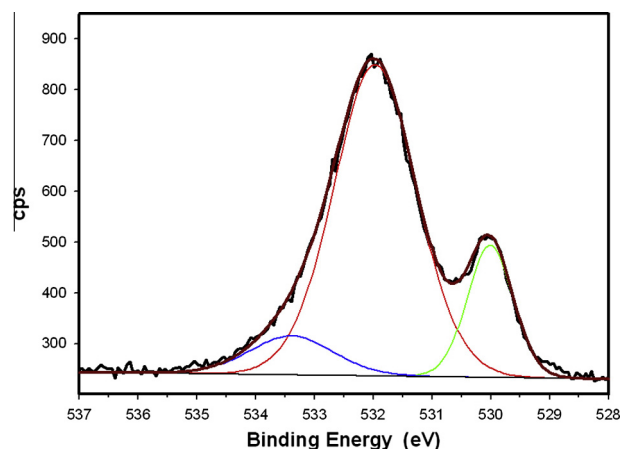


**Fig. 5.** O1s XPS-spectrum from Cu exposed to distilled water for 18,800 h (analysis performed in Ottawa).
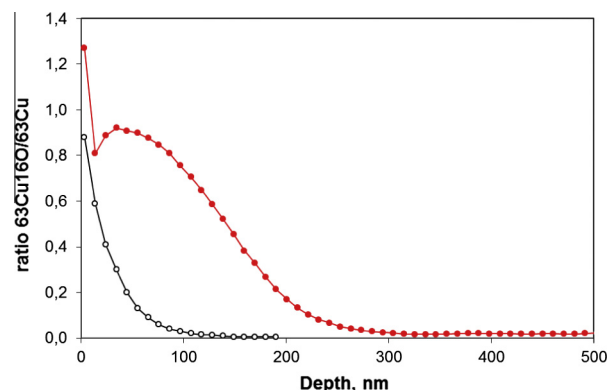


**Fig. 6.** Dynamic SIMS analysis of oxygen in outer part of Cu-samples. Black/open 3 years in air and red/filled 1 year in air plus 2 years in liquid water in the absence of $O_2$. (Analysis performed in Ottawa.) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

### 3.3. Hydrogen-uptake in corrosion of copper in oxygen-free water

A commonly held view is that no reaction or a reaction limited to the first atomic surface layer takes place when copper is exposed to $O_2$-free water, and that the reaction product, if present, is CuO or $Cu_2O$. Hydrogen production during the corrosion process is ignored. The fact that copper hydroxide is thermodynamically more stable than the hydrogen-free oxide [2] is neither widely known nor accepted. Fig. 10 illustrates our model showing the
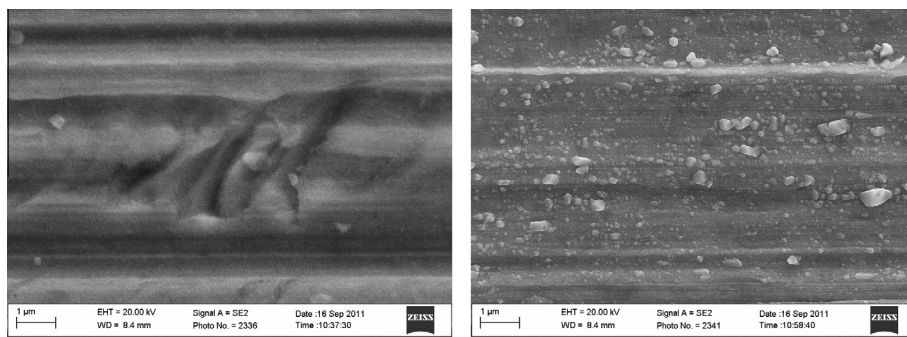


**Fig. 4.** FEG-SEM on Cu-samples. Left micrograph air exposed for more than 3 years at room temperature and right micrograph after 2.2 years in distilled water at 21–55 °C plus 0.5 year in air at room-temperature.
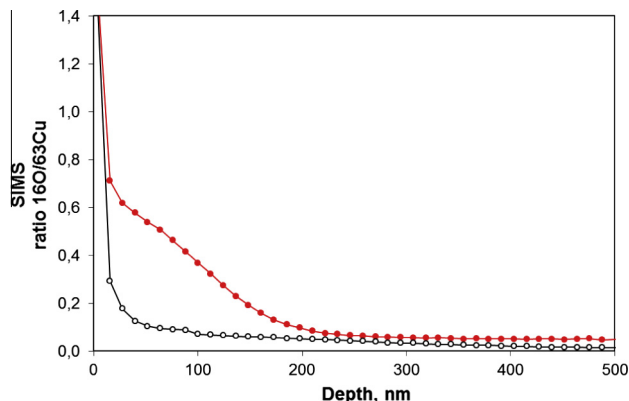
**Fig. 7.** Dynamic SIMS analysis of oxygen in outer part of Cu-samples. Black/open 3 years in air and red/filled 1 year in air plus 2 years in liquid water in the absence of $O_2$. (Analysis performed in Singapore.) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
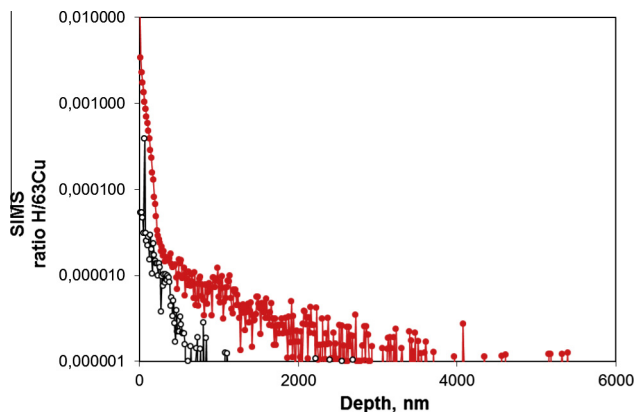


**Fig. 9b.** Desorption (outgassing) of water after different Cu-exposures. Measurements after 2 h desorption at each temperature. In total 12 h outgassing at each temperature.



**Fig. 8.** Hydrogen detection in SIMS. Black/open 3 years in air and red/filled 1 year in air plus 2 years in liquid water in the absence of $O_2$. (Analysis performed in Singapore.) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
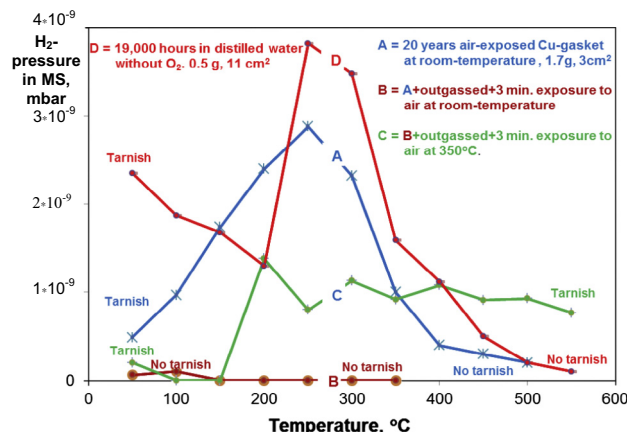


**Fig. 10.** Model for hydrogen-uptake in corrosion of copper in oxygen-free water.



**Fig. 9a.** Desorption (outgassing) of hydrogen after different Cu-exposures. Measurements after 2 h desorption at each temperature. In total 12 h outgassing at each temperature.

hydroxide corrosion product and hydrogen penetration into the grains and grain boundaries of the copper substrate.

The inward transport of hydrogen takes place mainly via interstitial diffusion. Hydrogen in Fig. 10 is located in various traps [11]
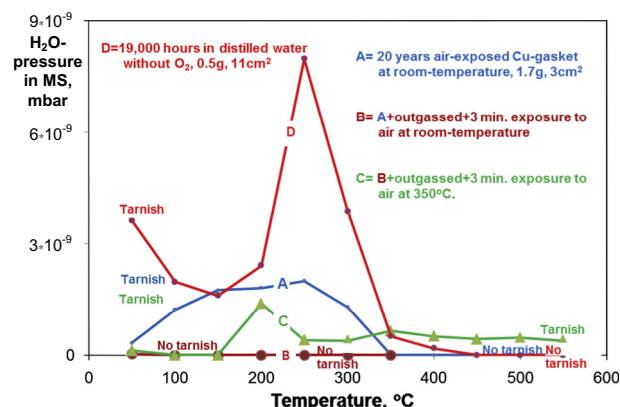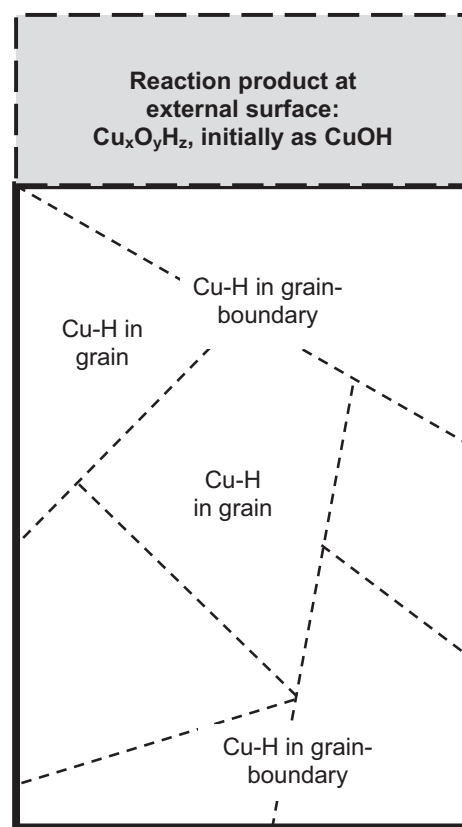
and the corresponding energies of these traps are, to our knowledge, not established but might well exceed the energy associated with diffusion. Vacancies in a poly-crystalline metal-sample cannot be avoided [16] and it has recently been found that they also trap hydrogen [17].

The model therefore takes into account hydrogen production and hydrogen uptake into the copper substrate. These are crucial for corrosion to occur. In keeping with this model, a defect-free copper single crystal without imperfections such as vacancies is unlikely to corrode in $O_2$-free water.

## 4. Conclusions

I. Cu reacts with water producing hydrogen as a by-product.

II. In the temperature range 22–56 °C there is a maximum hydrogen gas pressure which is interpreted as a balance between reaction product growth and removal (reduction) of the same reaction product.

III. Hydrogen can be detected in the Cu-metal from the reaction in I.

IV. A hydrogen-containing solid reaction product is formed during reaction of Cu by water which is characterized by SEM, XPS and SIMS.

V. Oxide grains up to approximately 0.5 μm are observed in SEM-micrographs.

VI. An analysis of binding energies in XPS strongly indicates a reaction product containing both hydroxide and oxide.

VII. Depth profiles in SIMS show that oxygen is mainly present in the outer 0.3 μm and hydrogen is well below the oxygen.

VIII. The reaction product formed on Cu in exposure to air at 350 °C is more stable in ultra high vacuum above 300 °C compared with the reaction product formed near room-temperature in water, with or without $O_2$.

## Acknowledgement

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