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Hydrogen gas production during corrosion of copper by water

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ABSTRACT

This paper considers the corrosion of copper in water by: (1) short term, open system weight measurements and (2) long term, closed system immersion in distilled water (13,800 h) without O_2 at 21–55 °C. In the latter experiments, the hydrogen gas pressure is measured above the immersed copper and approaches $\sim 10^{-3}$ bar at equilibrium. This pressure is mostly due to copper corrosion and greatly exceeds that in ambient air. Accordingly, this measured hydrogen pressure from copper corrosion increases with temperature and has the same dependency as the concentration of OH^- in the ion product $[OH^-]$ $[H^+]$.

1. Introduction

Due to the growth of visible reaction products the tarnish on copper-based materials needs to be removed in order to keep them shiny over the years. Most corrosion studies of copper have been performed in contact with air in our atmosphere. An exposure to hydrogen gas at atmospheric pressure is a well-known way to avoid tarnish on pure copper immersed in deionised liquid water and it is sometimes believed, but experimentally unsupported, that water itself will not corrode copper. This belief often comes from that hydrogen-free copper oxides can only exist near room-temperature below a certain hydrogen activity and it is assumed that this hydrogen activity is approximately the same as the hydrogen gas pressure. The hydrogen gas pressure in our atmosphere has been tabulated as 5×10^{-7} bar and is obviously far from atmospheric pressure. To understand the corrosion of copper in water we need to consider several issues including the activity of hydrogen gas and the operative reaction product. The main aim of this publication is to determine the pressure of hydrogen gas required to avoid tarnish of polycrystalline copper in liquid distilled water at different temperatures.

Results of hydrogen gas release from copper corrosion in distilled water were originally published 25 years ago in this journal [1] and followed up in recent publications [2,3]. We believe that knowledge of corrosion of copper as well as implications from various applications can be gained from the present study. For clarity we use the terms molecular hydrogen or hydrogen gas for H_2, the word hydrogen for H and analogously for oxygen. Consequently, with these terms water contains both oxygen and hydrogen. Liquid water furthermore contains H^+ and OH^- ions via partial dissociation (autoprotolysis) of the water molecule. Therefore liquid water facilitates the supply of a corrosion couple where CuH and CuOH are possible precursors or end products. This approach was taken thirty years ago in studies of water reactions on different crystallographic surfaces on metals with analysis techniques based on ultra high vacuum [4,5] and was later used in potential-pH diagrams [6].

Oxygen in the reaction product on copper also originates from water in a gas mixture with equal amounts of O_2 and H_2O but no attempt was made in that study to characterise the corrosion product [7]. It is generally observed that the 3-dimensional hydroxide $Cu(OH)_2$ is found and it is often believed that the mono-valent CuOH can only exist in 2-dimensional layers. However, we expect also CuOH to exist in 3-dimensional structures under certain conditions [3]. Obviously there is a need for an *in situ* method for characterisation of reaction products also in surfaces like grain-boundaries under relevant conditions. Such a characterisation is difficult, however, and not attempted here. To fulfil the main aim of this publication we discuss and interpret new detailed results of hydrogen gas detection in corrosion of Cu by liquid water at different temperatures. This hydrogen production takes place without any applied potential.

2. Experimental

In experiments described here, ≥99.95 wt%, OFHC-Cu with an as received surface finish has been used in hard or tempered con-

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dition in the form of 0.1 mm thick foils with average grain size of approximately 20 μm. Rods with 2 mm diameter of 99.995 wt%, OFHC-Cu ground to 1200 mesh with SiC paper have also been used in exposures of samples for 15 years in Fig. 7.

Fig. 1 shows a sketch of the experimental arrangement for quantitative detection, in the form of pressures of hydrogen gas in immersion of 140 cm^2 Cu. Apart from Cu, the closed system contained 0.1 mm thick, 17 mm diameter, >99 wt% palladium (Pd), 250 cm^2 stainless steel (SS) 316L in the ultra high vacuum system and 90 cm^3 of distilled water. Pd serves here as a membrane and separates hydrogen gas from water vapour [8]. The absolute pressure meter below the membrane is used for determination of temperature via the well-established influence of temperature on the water vapour pressure. This meter measures total pressure, but the contribution of H_2 to the total pressure is measured above the membrane. Therefore the meter below the membrane is suitable for temperature determination.

In the exposure with results presented in Figs. 4a and 4b dissolved air in the distilled water was in the start of the exposure removed by repeated evacuation 14 times of the gas phase volume above the liquid water [3]. A slight boiling of the water during the approximately 10 s evacuation increased the rate of gas removal. This procedure of evacuations took in all approximately 10 h.

Secondary ion mass spectrometry, SIMS, was used with a primary 4 keV Cs^- ion beam, and secondary ions from approximately 100 μm × 100 μm were detected with results shown in Figs. 6 and 7. In the short time exposure with NaOH addition to distilled water at room-temperature, the sample was carefully polished down to submicron flatness to optimize depth resolution of the formed reaction product in the subsequent SIMS analysis.

3. Background results

The corrosion rate can be found in weight loss measurements where the dissolution of the solid reaction product can be an approximate measure of corrosion of the metal. This takes place at a sufficient amount of water in the exposure of the metal where any suppression of corrosion rate, due to formation of a solid reaction product, is negligible.

Fig. 2 shows how the amount of water per time unit and Cu-surface influences the weight of Cu in water exposure. Obviously we can expect a weight gain or a weight loss depending on the access of water. This phenomenon is simply explained by one rate for reaction product dissolution and another rate for formation of the reaction product. In atmospheric corrosion without any precipitation we expect a weight gain of Cu.

The influence of the concentration of protons on the corrosion rate of Cu is seen in Fig. 3. By necessity other ions apart from OH^- are needed for a variation of the concentration of protons. The variation of proton (H^+) concentration was obtained by additions of NaOH or HCl to 5 dm^3 distilled water. At room-temperature only a proton concentration of 10^{-7} mol l^{-1} water can be obtained without additions of other ions. We interpret the phenomenological role of proton concentration (pH) in Fig. 3 as:

(a) at high concentrations of protons, pH 0–4, protons will be consumed and replaced by positive Cu-containing ions;
(b) at medium concentrations of protons, pH 5–8, the supply of protons comes from partial dissociation of water:

$$H_2O \rightleftarrows H^+ + OH^-$$

(c) at low concentrations of protons, pH 13–14, the un-dissociated water molecules supply protons.

Bubbling of oxygen gas, shown in Fig. 3, has an effect on the corrosion rate of Cu only at high consumption rates of protons, which takes place at pH 2–4 in this figure. This bubbling can then be rate-determining for the corrosion rate. In Ref. [9], results are presented from dissociation measurements of molecular oxygen at $p_{O_2} = 20$ mbar on different materials and it is found that there is a huge variation of the dissociation ability among different materials and also the most well-known catalysts platinum and ruthenium dissociate O_2 far less than what is theoretically possible. Actually, on average only one in 10^{11} impinging O_2-molecules on the surface dissociate to atomic oxygen ($O_2 \rightarrow 2O$) near room-temperature. Naturally, the rate of H_2-dissociation also varies among different materials [10,11] although, to our knowledge, not many materials have been studied [12].

4. Present results and general discussion

4.1. Measurements of H_2

Air is initially removed in the studied system as described in reference [3]. The main aim here is to measure the H_2-pressure from Cu corrosion in distilled water. Fig. 4a shows the detected H_2-pressure from 4800 to 8800 h and Fig. 4b from 8800 to

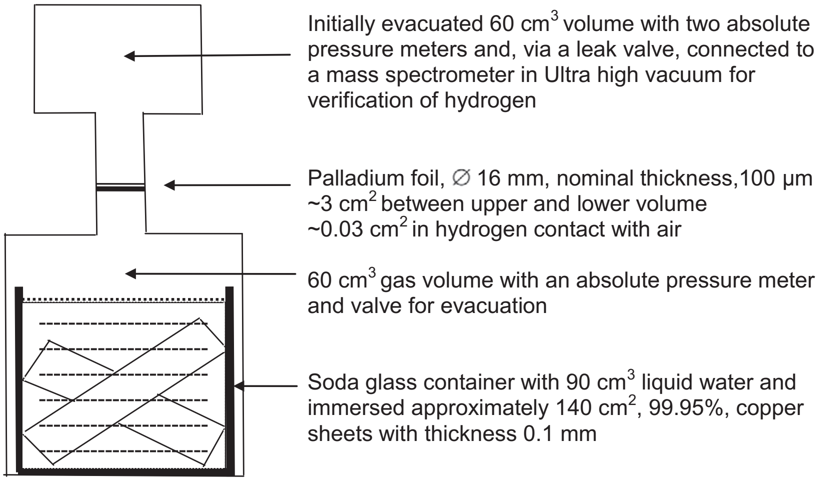

Fig. 1. Sketch of equipment used for studies of hydrogen evolution in Cu corrosion in distilled liquid water. Equipment of stainless steel 316L and ultra high vacuum gaskets of Cu with approximately 2 cm^2 area.