COMMENTS ON HYDROGEN EVOLUTION FROM THE CORROSION OF PURE COPPER

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Abstract—Some comments are given on the experimental conditions in two recent communications in this journal which deal with copper corrosion in water. Also some additional experimental information and thermodynamic considerations on a possible hydrogen release from copper in water is given, including a very simple and straightforward experiment.

INTRODUCTION

THE EXPERIMENTAL results on hydrogen release from the corrosion of copper in water in communications[1] and[2] seem to be in total contradiction. The reason for this might be found in differences in the experimental conditions shown in Table 1. Some comments on the differences are given here but also the results from some additional experiments and thermodynamic considerations are presented.

SOME DIFFERENCES IN EXPERIMENTAL CONDITIONS

Surface finish of copper

The same bulk copper material seems to have been used in both studies but the surface finish was probably different. A smoother, air-formed oxide, could have been present in Ref. 1 while a relatively rough oxide-free surface, was used in Ref. 2. In the production process of the copper sheets, bright annealing in a hydrogen atmosphere could have been used. In such a case hydrogen might have been introduced in a thin surface zone which could have suppressed the corrosion of the metal in Ref. 1 if this zone was not removed.

Composition of solution

In Ref. 1 0.3 l of water containing 8 g l^{-1} NaCl was used and in Ref. 2 1.2 l distilled water. The NaCl addition will increase the amount of copper going into solution which could increase the pH leading to a lower corrosion rate. The protective properties of the reaction products adhering to the copper surface can be different in the two solutions.

TABLE 1.   SOME EXPERIMENTAL CONDITIONS AND RESULTS PRESENTED IN REF. 1 AND REF. 2

Conditions/results	Ref. 1	Ref. 2
Solution	8000 mg l^{-1} NaCl	distilled water
Volume of solution	0.3 l	1.2 l
Temperature	50 and 80°C	25°C
Duration	1008 h	1100 h
Technique for hydrogen detection	gas chromatography	electrolyte probe
Form of hydrogen detected	molecular	atomic and molecular
Oxygen conc. in gas at start of experiment	<2 vol. ppm	20 vol.%
Oxygen conc. in gas at end of experiment	—	—
Hydrogen conc. in gas at end of experiment	<1 vol. ppm	30 vol.%
Purity of copper used	>99.7%	>99.7%
Copper surface area	2400 cm^2	1460 cm^2
Surface finish of copper	—	mech. pol. 800 mesh SiC paper
Weight change of copper	loss 0.4 ± 0.5 mg	gain 21.2 ± 0.5 mg
Copper content in solution at end of experiment	—	<0.5 mg

Technique for hydrogen detection and presence of oxygen

In Ref. 2 a solid electrolyte probe involving a palladium working electrode was used. The cause of the first potential rise (from −80 to ~100 mV) can only be understood by considering the palladium surface properties in the probe. In Ref. 3 the H_2–O_2 reaction was studied on palladium. A potential shift of ~200 mV was attributed to oxygen present at constant hydrogen concentrations. Also according to the calibration, where no oxygen (<1 ppm) was present in the mixed gases, 1 ppm hydrogen corresponded to ~90 mV while the starting potential was ~ −80 mV in the copper corrosion study. We disagree with the interpretation made in Ref. 1 that 2 × 10^{-6} bar of oxygen is insufficient to prevent a possible hydrogen release. From Ref. 2 we can hardly calculate the actual oxygen concentration at the copper surface when the hydrogen concentration exceeds, for example, 1 ppm in the gas volume above the water level. Instead we can make a conservative estimate by assuming a sticking probability for oxygen of unity. This would show that only ~2 ppb of oxygen need to be present in the water at room temperature to consume hydrogen ($2H + \frac{1}{2}O_2 \rightarrow H_2O$) at a metal corrosion rate of 0.1 μg cm^{-2} h^{-1}. This means that 2 ppm oxygen in a gas volume above the water at elevated temperature might be sufficient to prevent hydrogen release from the corroding surface at a slightly lower corrosion rate than 0.1 μg cm^{-2} h^{-1}. We do not claim that this is the case in Ref. 1 but it cannot be ruled out completely.

The same probe used for the study of copper corrosion has also been used for measuring hydrogen release during zinc corrosion in pure water.[4] A constant release rate of 17 ng cm^{-2} h^{-1} was found after an initial time period without hydrogen release. In the same study a simple experimental arrangement with a manometer for the study of zinc corrosion showed an initial pressure decrease followed by a constant increase which corresponded to 12 ng cm^{-2} h^{-1} of hydrogen. This agreement in evolution rates for zinc indicates that the probe used in Ref. 2 together with its calibration *is relatively reliable.*

The copper content in solution at the end of the experiment

In Ref. 2 a concentration of <0.5 mg l^{-1} is reported (the actual concentration in that specific experiment was 0.17 mg l^{-1}). In Ref. 1 no analysis of the solution seems to have been performed. Obviously, an experimental value of the copper content in the solution could offer an independent determination of the average corrosion rate when the weight gain/loss is known and the adhering reaction products are identified.

ADDITIONAL EXPERIMENTAL INFORMATION ON HYDROGEN RELEASE FROM COPPER CORROSION IN WATER

The approach of a very simple and straightforward type of qualitative experiments is presented here. These experiments require a minimum of experimental facilities and the only detector used is the human eye. The experiments comprise the arrangement of two corroding systems with copper and water. One system is closed with respect to oxygen but relatively open with respect to hydrogen while the other is closed with respect to both oxygen and hydrogen. Since most of the corrosion of copper in distilled water produces solid reaction products (in the form $Cu_xO_y(OH)_zH_v$) a visual inspection can reveal any eventual difference in the degree of copper corrosion taking place in the two systems described above.

One experiment of this kind is presented in Fig. 1, where 5.8 cm^2 of mechanically polished OFHC copper, 1.7 ml distilled water and $27 \pm 5 \, \mu g$ of oxygen were present in the two systems at the time of closure at 50°C. The only difference between the systems was that palladium was used as the upper enclosure of one system and platinum as the upper enclosure of the other. It is well established that the diffusion of hydrogen in palladium greatly exceeds that in platinum.[5] By visual inspection every 50 h a gradual change in the appearance of the copper surfaces could be observed to take place in both the systems. Up to ~200 h the change in colour took place in both the systems with no significant difference between them. During this time period the $27 \pm 5 \, \mu g$ oxygen was most likely consumed and some hydrogen produced. During the time ~200 to ~3000 h only the copper present in the system with the partial palladium enclosure changed in colour. After ~3000 h some of the copper rods were analysed in an ESCA spectrometer with ion etching facilities. From this analysis the thickness of corrosion products, which was mainly Cu_2O on all surfaces, was 5–6 times greater on the copper rods from the system with partial
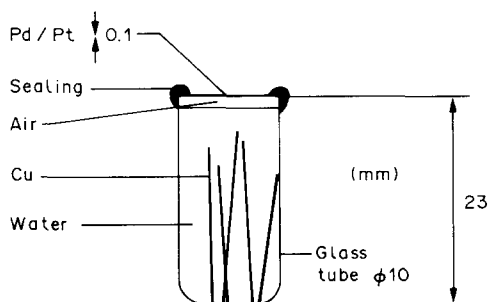

FIG. 1.   Experimental arrangement for study of copper corrosion.

TABLE 2.   RELATIVE ABUNDANCES OF SPECIES FROM CORROSION PRODUCTS FORMED UPON EXPOSURE OF Cu. SIMS Ar^+, 3 nA, 6 kV, 10^{-4} cm^2

CuH^+	CuO^+	$CuOH^+$	Cu_2O^+	Cu_2OH^+	Exposure
<2.3	9.0	4.5	62.4	21.8	800 h dist. water in air contact RT
28.6	9.3	14.9	31.1	16.1	3000 h dist. water Pd enclosed 50°C + stored in air 5000 h at RT
28.2	9.4	15.4	29.9	17.1	3000 h dist. water Pt enclosed 50°C + stored in air 5000 h at RT

palladium enclosure. We judge that this experiment shows that mechanically polished OFHC copper continues to corrode in distilled water also after atmospheric oxygen has been consumed. The kinetics of this corrosion can be ruled by diffusion of hydrogen through the enclosure of the system.

A shortcoming of the ESCA technique is its inability to probe hydrogen. However with Secondary Ion Mass Spectrometry (SIMS) this can be done[6] by monitoring the ratio of metal–hydride to metal ion emission MeH^+/Me^+. For this reason the corrosion products on the copper rods were analysed by SIMS and compared with the analysis of corrosion products on copper which had been immersed in distilled water in air contact (Table 2).

There is a considerable difference in composition of the corrosion products when atmospheric oxygen is present compared to when it is not. The higher $CuOH^+$ values in absence of atmospheric oxygen are accompanied by the higher CuH^+ values. The high CuH^+ values were found also beneath the visible reaction product, i.e. in the metal region, down to a depth of $\sim 1\,\mu m$. Also in this SIMS analysis the thickness of corrosion products was ~6 times greater on the rods from the partial palladium enclosed system.

In Fig. 2 a similar experimental arrangement to that in Fig. 1 is shown, but facilities for potential measurements are included. The palladium sheet allows hydrogen to escape from the lower system and combine with oxygen at the upper water/palladium interface. The potential as measured in Fig. 2 is influenced by hydrogen at this interface. Four glass tubes with distilled water were prepared containing 70 cm^2 of OFHC copper, 30 cm^2 of iron, 30 cm^2 of zinc and without any metal, respectively. The same saturated calomel electrode and the same Pt-tip (<1 mm^2 area facing the water) were used in all potential measurements. The palladium sheets were mechanically polished before closure of the systems. The four experimental arrangements were placed close together in the laboratory to minimize differences in temperature (room temperature) and air composition. Potentials measured from the systems containing the metals were compared with the potential from the empty (only water containing) system. In this way the potential change due to metal corrosion in the systems could be extracted. The results are, of course, only qualitative but suggest a sensitive method for studies of hydrogen release in various corrosion processes.
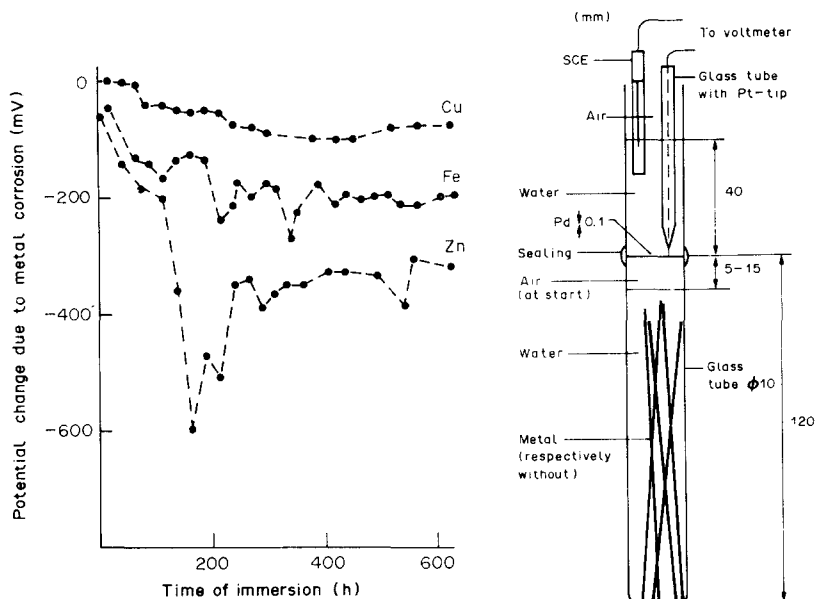
FIG. 2. Experimental arrangement for study of metal corrosion and the results from a study of copper, iron and zinc.

PRIMARY REACTIONS IN THE METAL–WATER SYSTEM AND SOME THERMODYNAMIC CONSIDERATIONS

The corrosion rate of a metal is the amount of metal leaving its metallic state per time unit.[7] The value of the concept of applying a thermodynamic forecast of the maximum degree of corrosion is limited to well defined reaction products and their thermodynamic data. For example, the results presented in Table 2 imply that the equilibrium molecular hydrogen concentration calculated according to:

$$H_2O + 2Cu \leftrightarrows Cu_2O + H_2 \tag{1}$$
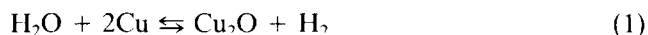
is not relevant for a system without atmospheric oxygen since the corrosion product formed in the absence of atmospheric oxygen is of a far more complex nature than Cu_2O.

The role of atmospheric oxygen in metal corrosion in water is still not well understood. An attempt to contribute to the knowledge of this relatively simple system has been made by probing hydrogen (molecular + atomic) in water exposure of Cu, Fe and Zn.[4] The conclusion in that study concerning hydrogen was that atomic and/or molecular hydrogen is released when copper, iron or zinc is immersed in water and that takes place mainly after atmospheric oxygen has been consumed.

We have tried further to clarify the primary reactions taking place during the exposure of Cu, Fe, Zn and Zr to water by using SIMS. In Table 3 results on detected species from Cu, Fe, Zn and Zr upon exposures of these metals to different gas compositions are presented. An increase in the $MeOH^+$ species is found upon water

TABLE 3. NORMALIZED INTENSITIES MeX^+/Me^+ OF SPECIES DETECTED UPON EXPOSURES OF Zr, Zn, Fe AND Cu METALS TO VARIOUS GASES. SIMS Ar^+ 6 kV 3 nA 10^{-1} cm^2
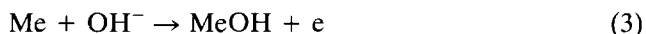
						Gas composition (mbar)		
ZrH^+	ZrO^+	$ZrOH^+$	ZnH^+	ZnO^+	$ZnOH^+$	H_2	H_2O	O_2
0.045	1.73	0.860	0.42	0.026	0.137	3×10^{-9}	1×10^{-7}	5×10^{-11}
0.063	0.63	0.009	0.19	0.023	0.023	1×10^{-7}	1×10^{-9}	4×10^{-12}
0.039	0.72	0.007	0.07	0.021	0.026	2×10^{-9}	2×10^{-9}	1×10^{-7}
FeH^+	FeO^+	$FeOH^+$	CuH^+	CuO^+	$CuOH^+$	H_2	H_2O	O_2
0.049	0.0055	0.022	0.0029	0.0005	0.0029	3×10^{-9}	1×10^{-7}	5×10^{-11}
0.006	0.0089	0.003	0.0015	0.0005	0.0010	1×10^{-7}	1×10^{-9}	4×10^{-12}
0.005	0.0018	0.004	0.0004	0.0015	0.0008	2×10^{-9}	2×10^{-9}	1×10^{-7}

exposure. This is the case for all the four metals. Furthermore it should be noted that ZnH^+, FeH^+ and CuH^+ values are higher in water exposure than in H_2 exposure. Upon oxygen exposure the lowest values of MeH^+ appear for all the metals studied.

Based on these results and from other studies[2,4,8] we find that the primary reaction steps for copper exposed to water are in accordance with the general description:

$$Me + H_2O \rightarrow Me(H_2O)_{ads} \rightarrow MeOH + H \tag{2}$$

or in the terminology of electrochemistry

$$Me + OH^- \rightarrow MeOH + e \tag{3}$$

$$H^+ + e \rightarrow H. \tag{4}$$

Since we also find Cu_2OH^+ species in addition to $CuOH^+$ upon water exposure of copper in SIMS[9] we also consider:

$$2Cu + H_2O \rightarrow 2Cu(H_2O)_{ads} \rightarrow Cu_2OH + H \tag{5}$$
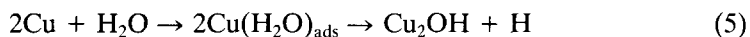
as a primary reaction for copper exposed to water.
For copper step (2) can be followed by

$$2CuOH \rightarrow Cu_2O + H_2O \tag{6}$$

or

$$CuOH \rightarrow CuO + H \tag{7}$$

and (5) can be followed by

$$Cu_2OH \rightarrow Cu_2O + H. \tag{8}$$
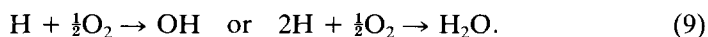
In general the atomic hydrogen formed in (4), (5), (7) and (8) can follow various pathways:

(i) Atomic hydrogen can combine with atmospheric oxygen at surface sites:

$$H + \tfrac{1}{2}O_2 \rightarrow OH \quad or \quad 2H + \tfrac{1}{2}O_2 \rightarrow H_2O. \tag{9}$$

(ii) Atomic hydrogen can form molecular hydrogen at surface sites:

$$H + H \rightarrow H_2. \tag{10}$$

(iii) Atomic hydrogen can enter the metal Me.

(iv) Atomic hydrogen can, via surface diffusion and/or desorption, reach other material and further via volume diffusion escape from the corroding system if this material constitutes the enclosure of the system.

The equilibrium between atomic and molecular hydrogen in the gas phase is $\sim 1:10^{35}$ which means that upon H_2 exposure the activity of atomic hydrogen on a surface is crucially dependent upon the ability of the surface to dissociate molecular hydrogen to atomic hydrogen. According to Ref. 10 copper does not dissociate molecular hydrogen on low index single crystal surfaces. It is also evident in Table 3 that the activity of hydrogen on copper upon exposure to 10^{-7} mbar molecular hydrogen is insufficient to prevent CuOH formation.

In ref. 2 an attempt was made to calculate the position on the hydrogen scale of a modified reversible hydrogen electrode:

$$H^+ + e \leftrightarrows H \leftrightarrows \tfrac{1}{2}H_2 \tag{11}$$

in which the H_2 concentration equals the H_2 concentration in (sea) water, in air contact, and for reactions involving *one* electron transfer as in (4). A displacement of $9 \times 60 = 540$ mV of the hydrogen electrode in the potential $-$pH diagram was mentioned which means 120 mV vs SHE at pH 7 while $9 \times 30 = 270$ mV displacement corresponds to reactions like (1). The oxidation potential for copper to Cu_2O is <120 mV vs SHE at pH 7. Certainly the oxidation potential for the complex reaction product found in Table 2 is lower than 120 mV which means that the corrosion of copper in pure water is thermodynamically possible when considering one electron process. This supports the conclusions made in Ref. 2 which were mainly based on experimental findings.

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