



Contents lists available at ScienceDirect

## Corrosion Science

journal homepage: [www.elsevier.com/locate/corsci](http://www.elsevier.com/locate/corsci)

## Correspondence

Response to the comments by P. Szakálos, T. Åkermark and C. Leygraf on the paper “Copper in ultrapure water, a scientific issue under debate”

## ARTICLE INFO

## Keywords:

- A. Copper
- B. XPS
- C. AES
- D. Oxidation

## 1. Introduction

Szakálos et al. [1] have made serious remarks and insinuations that our work concerning the extent of copper corrosion in anoxic ultrapure water is misleading, owing to inappropriate experimental procedures and faulty equipment. Their comments also contain references to details taken from intermittent reports made during the long term study of the subject, thereby including preliminary and even discarded results or methods.

## 1.1. The project and its development

In this project, spanning over several years, two different approaches were followed simultaneously to develop a fuller picture of a possible reaction between copper and water. One direction concerned oxidation (from “open” systems) and one reduction (from “closed” systems). An overview and partial results from this long-term study were published previously [3]. Our latest results [2] are focused on the possible oxidation of copper.

All materials chosen were scrutinised beforehand, as well as the experimental methodology, through extensive literature research, consultations with colleagues and testing. For instance, we compared different stainless steel and glass qualities, when deciding on the choice of test container materials. Various methods were considered for solving delicate analysis problems, and purification methods were compared critically, such as for removing oxygen dissolved in water, hydrogen present in copper, and for creating a clean copper surface. Mechanical polishing was abandoned because of the surface contamination risk as well as the inevitable introduction of microstructure modifications. Electron spectroscopies were chosen to yield satisfactory surface analysis, in particular for oxidation products on copper. This ongoing “work-in-progress” after the planning stages during some years entailed the production of several interim reports to SKB [4] and resulted in two scientific publications [2,3].

We performed the work in a controlled atmosphere (by using a glove box, UHV, transfer vessel), being extremely careful as regards contamination risks during transfer of specimens to and from analysis instruments. Szakálos et al. [1] have chosen not to comment on any chemical analyses made despite the crucial outcome that no appreciable amounts of oxidation species are found on the copper surface or in the near environment (glass, water). The comments thus do not discuss the main focus of our contribution [2], *i.e.* the analyses and their consequences. Instead, criticism is made on practice and results presented in various SKB reports that also contain preliminary, intermediate and not yet analysed results, including observations and methods that we later judged as being inconsistent or too inferior to belong to a final scientific paper.

## 2. Discussion

Corrosion is a redox process, which means that any reduction of water must be accompanied by a corresponding oxidation of the metal, a connection that cannot be circumvented. This twin reaction initiated a dedicated study of the state of the copper, searching for evidence of copper oxidation products. This is a very important aspect, in fact a crucial one, yet in general neglected in other studies of copper corrosion in water. Eventually, we chose to present only such findings in Corrosion Science [2], a decision taken after analysing the hydrogen pressure increase further and allowing a longer time span for the oxidation studies [3]. Our conclusion concerning the corrosion issue is therefore based on more solid evidence than can be gained from hydrogen pressure measurements, which are easily affected by external hydrogen sources. The implicit very low hydrogen pressure, considering the hereby well-established very low oxide production, sets extremely harsh conditions on the equipment. Although the steel can be baked out to lower the hydrogen background, the pressure gauges (which cannot be baked out) still contribute to the hydrogen background pressure. If underestimated or even neglected, such sources yield hydrogen values that may erroneously be interpreted as corresponding to extended corrosion, without any corresponding amounts of oxidation products (and then oxygen contamination must be strictly precluded). Our main conclusion from our analysis of this matter, that pressure measurements are vulnerable to interference, has been transformed by Szakálos et al.

<https://doi.org/10.1016/j.corsci.2018.02.003>

Received 25 June 2017

0010-938X/ © 2018 Elsevier Ltd. All rights reserved.

[1] to infer that we “admit that the experimental conditions are insufficient [...] due to the high background pressure”. That statement is not correct.

They argue that we have failed to fulfil some experimental prerequisites that they define as fundamental, and conclude that our results are based on a “flawed experiment” with regard to copper pre-treatment as well as the monitoring of hydrogen pressure. That latter issue (see above) is not related to the kinds of investigations (effects of oxidation from “open systems”) presented in our recent article [2]. Similarly, some references given by Szakálos et al. are not directly related to our text, contain misunderstandings or are even coloured by preconception of facts. Their main pieces of criticism concern *i*) oxygen control; *ii*) hydrogen control; *iii*) copper surface pre-treatment. At the end they give examples of other studies where copper corrosion is claimed to occur – which again is not a direct comment on our findings. We choose to treat the three items in a different order, starting with hydrogen control, even though that plays a minor role for our conclusions.

## 2.1. Hydrogen control

Our article is focused on the formation of copper oxidation products, mainly acquired from open systems. We are nevertheless forced to react strongly to the statement that “the authors admit that the experimental conditions are insufficient”, a phrase that is further connected to the allegation that we had a “high background pressure” of 0.7 mbar, this value being so high that “any copper corrosion in anoxic water would be inhibited”. However, to say that this figure represents the pressure during the series of experiments is an obvious misinterpretation of a certain test experiment. The palladium membrane that covers the steel container faces the outside atmosphere (glove box) and allows any evolved hydrogen to pass freely through it. There will be an initial increase before the steady-state pressure is attained, at which the diffusion rate through the membrane will be the same as the hydrogen outgassing/production rate. Typical values for a steady-state pressure were measured independently for several months before starting the long-term experiment series: for such an “open” setup it was 0.004–0.013 mbar, with the membrane in contact with air and 0.003–0.006 mbar in the N<sub>2</sub>-filled glove box [4]. These values are two orders of magnitude lower than the “equilibrium hydrogen pressure for anoxic copper corrosion” of 0.1–1 mbar claimed in the comments by Szakálos et al. [1,5,6]. The “paramount importance” of low background pressure was thus ensured in our experiments and, referring to their caution, its value could not have impeded anaerobic copper corrosion. It is noteworthy that pressures as high as 0.1–1 mbar above the background would have been easily measured by our equipment (“closed systems”), which is described as being part of “a flawed experiment”. We would in that case certainly also have registered appreciable effects of the corresponding oxidation. In our experiments we did not observe Cu<sub>2</sub>O, CuO nor Cu(OH)<sub>2</sub>.

We have stated [2] that pressure measurements (reflecting the reduction reaction of corrosion) are not a valid method for establishing a true picture of the corrosion situation because of the hydrogen content of the stainless steel and the emission from other parts of the equipment. We have used 304L stainless steel, a material that is commonly used for UHV chambers as for various fittings. Stainless steel always contains dissolved hydrogen that leads to spontaneous constant outgassing [7]. The hydrogen outgassing rates for 304L and 316L steels are about  $3 \cdot 10^{-11}$  Torr/L/s/cm<sup>2</sup> after a standard bake out at 150 °C. For an overview, see table 1 (with references), included to allow for a rapid consultation. The authors of the Comments claim that the 316L is to be preferred to 304L, but they do not give any reference to support such a statement; they actually only refer to their own work where such properties are neither compared nor tested.

In contrast, we did investigate the outgassing rate from the setups (made from 304L stainless steel). Considerable effort was expended to reduce the outgassing further by enhanced bakeout (at 450 °C), although the original values were actually quite in line with those found in the literature (See Table 1). We also investigated and modelled the influence on pressure by the hydrogen uptake of the palladium membrane. For pressures lower than 0.02 mbar, the outgassing rate will be strongly underestimated by neglecting the hydrogen uptake by the Pd membrane [4]. Moreover, we have measured the outgassing rates from an empty system (without Pd membrane and water) and compared the result with the pressure increase for the same system with membrane and water included. No significant difference was observed between the vacuum test values and the water/Pd backgrounds. Hence, no increased background hydrogen gas pressure could be observed due to any corrosion reaction between water and the 304L stainless steel chamber. Therefore, we can exclude the suggestion that different corrosion resistance of the different kinds of steel would have any impact here. Moreover, the steel was never in contact with the liquid water in the glass beaker. The 316L steel is used for reducing pitting corrosion, mainly in seawater (containing Cl<sup>-</sup>) and in acid solutions. Since our water contains extremely low levels of chloride (ultra-pure, “ppt quality”) and has a pH close to 7, this type of corrosion is unlikely and may be disregarded. All these aspects were already clearly presented in our article [2].

We may use typical hydrogen outgassing data from the literature (Table 1) for an illustrative “thought experiment” (*Gedankenexperiment*). Suppose that, instead of outgassing, the very same evolution of hydrogen were a result of copper corrosion: the given rate of  $3 \cdot 10^{-11}$  Torr/L/s/cm<sup>2</sup> would then, for a copper surface area of 100 cm<sup>2</sup>, correspond to a corrosion rate of 0.3 μm/year. This means that the effects of outgassing cannot be neglected and that careful background measurements are mandatory. We note, from thorough analyses of copper oxidation products by various techniques, an estimated corrosion rate < 0.3 nm/year [2]. This value therefore corresponds to a hydrogen evolution that is far lower than the typical background. This example suggests that only unrealistically low background outgassing rates in stainless steel will enable the detection of the hydrogen emanating from copper corrosion.

**Table 1**  
Hydrogen background levels from outgassing.

Setup/components	Outgassing (Torr/L/s/cm <sup>2</sup> )	Mol/year (600 cm <sup>2</sup> surface area)
Typical data for 304 L, bakeout at 150 °C	About $3 \times 10^{-11}$ [8,9]	–
Typical data for 316 L, bakeout at 150 °C	About $3 \times 10^{-11}$ [8,9]	–
Our setup, bakeout at 150 °C	$2\text{--}3 \times 10^{-11}$ [10]	$3 \times 10^{-5}$
Our setup, bakeout at 450 °C	$2 \times 10^{-12}$ [10]	$2\text{--}3 \times 10^{-6}$
Pressure gauge MKS627B	–	$3 \times 10^{-6}$ [4]
Pressure gauge Pfeiffer CCR374	–	$1.1 \times 10^{-7}$ [4]

Download English Version:

<https://daneshyari.com/en/article/8955350>

Download Persian Version:

<https://daneshyari.com/article/8955350>

[Daneshyari.com](https://daneshyari.com)