Comment on "Penetration of corrosive species into copper exposed to simulated O₂-free groundwater by time-of-flight secondary ion mass spectrometry (ToF-SIMS)"

1. Introduction

In a paper entitled "Penetration of corrosive species into copper exposed to simulated O₂-free groundwater by time-of-flight secondary ion mass spectrometry (ToF-SIMS)", Yue et al. [1] have exposed oxygen-free phosphorous doped copper samples to simulated anoxic groundwaters, with and without 0.001 M sulfide, for periods of either 4 or 9 months. ToF-SIMS profiling was used to determine corrosion product thicknesses, reported to be between 7 and about 170 nm, and the extent of penetration into the copper samples, which was reported as being of the order of 100 nm at room temperature, and up to 400 nm at 60 °C. The species investigated were Cl, S, O, OH, and H. Bulk and grain boundary penetration rates were calculated, which for S (which seems to be the fastest species) were reported as 1.3 μm/yr and 1.5 μm/yr, respectively, at 60 °C. The relevance of the results for copper as a corrosion barrier in a geologic repository for spent nuclear fuel is discussed.

We have concerns *i*) about the fundamental interpretation of the ToF-SIMS data where it is claimed that a region of pronounced penetration into the metal exists under a thin layer of corrosion products and *ii*) about how the results are discussed in the context of geologic repository conditions.

2. Basic interpretation of ToF-SIMS data

A major concern about this paper is the authors' interpretation of their ToF-SIMS data as suggesting that there is, below a corrosion product film, a region of "pronounced penetration" where the corrosive species are said to be penetrating the metal, but apparently not causing corrosion at the metal surface. In our view, a much more straightforward interpretation, consistent with findings in other studies, would be that also this latter region is part of the corrosion product film.

Chen et al. [2] found a corrosion layer thickness of about one micrometer after a one month exposure of Cu to 0.001 M HS⁻ (at 25 ± 2 °C) whereas in the present study, exposure to the same sulfide concentration for several months resulted in considerably smaller thicknesses, also when the region of pronounced penetration is included.

Furthermore, the authors reference "the final project report" [3], in which gravimetric analysis has been performed for samples exposed to the same conditions as in the present article. The results for the pre-oxidized sample exposed to 0.001 M HS⁻ for 9 months yields an estimated corrosion rate of 0.29 μm/year, equivalent to a corrosion film thickness of roughly 430 nm after 9 months, taking the lower density of Cu in a Cu₂S film into account. This is more than the sum of the suggested corrosion product film thickness (27 nm) and the region of pronounced penetration (around 60 nm) in Fig 5, that shows ToF-SIMS depth profiles for a pre-oxidized sample exposed to the same conditions. For samples exposed to 0.001 M HS⁻ for 4 months at 60 °C, the measured corrosion rates are around 1.3 μm/year in Ref 3, whereas the suggested corrosion product film thickness after 4 months in Yue et al. is only 170 nm. Even the sum depth of the corrosion product film and the region of pronounced penetration, suggested to be around 450 nm after 4 months, corresponds to a corrosion rate substantially less than 1.3 μm/year when the lower density of Cu in the corrosion product film is taken into account. The results in Refs. 2 and 3 thus support the interpretation that the regions claimed to be exhibiting pronounced penetration into the base metal are in fact part of the corrosion films.

We do not see that the authors present any convincing evidence for the existence of a region of pronounced penetration. The interface between the corrosion product film and the region interpreted as pronounced penetration is defined at the highest point in the signal of either S or O. It is noted by the authors that there is no sharp boundary at the interface, which they suggest is a result of different corrosion rates for different grains. This, however, not explain the fact that the signal intensity of e.g., S is as high in the region of pronounced penetration as in the corrosion product layer. This latter fact is, in our view, a clear indication against the authors' interpretation. The signal intensity of S must be expected to decrease considerably when going from the corrosion layer to the metal bulk. We note that the shapes of the depth profiles of the elements of the corroding agents also in the regions of pronounced penetration are not incompatible with what could be expected in general for a corrosion product layer for a rough surface of a polycrystalline material, and thus not in conflict with our alternative interpretation.

We also note that effects of surface roughness are not discussed, but

simply dismissed as not having "any considerable effect on the interpretation of the ToF-SIMS data". Scratch marks from the polishing in e. g., Figs. 1 and 2 in Ref 1, together with the presented sample grinding to 600 grit, suggest a surface roughness in the order of at least 100 nm. Since the suggested penetration depths are much smaller than 100 nm, the surface roughness has likely influenced the measurements in a way that cannot be disregarded.

We find Fig. 12 in Ref. 1 quite misleading in terms of the scale of suggested penetration, even from the experiments, which only look at the very top surface, and not several hundreds of micrometers in depth, past several grains.

The authors' hypothesis that sharp curve features are blurred by the signal being an average of all exposed grains could have been tested by evaluating the depth data for a single grain, i.e. by constructing depth profiles of the types in Figs. 3a, 5a, 7 and 11 in Ref. 1 as sums over a single grain rather than over the entire sample. Already with the data presented in the paper we note that the structures of the reconstructed 3D images in Figs. 3b and 5b in Ref. 1 do not seem to reflect the grain locations in the corresponding Figs. 2 and 4 in Ref 1, contrary to what would be expected if the authors' suggested explanation were correct. Another obvious test would have been to perform ToF-SIMS analyses of samples from which the corrosion film has been removed, by e.g. the method used in Ref. 3. It is, furthermore, unfortunate that only one analysis technique was used in the examination of the corroded samples. Simple examination of cross sections with SEM could have shed more light on the question of the corrosion film thickness.

The authors' interpretation of the ToF-SIMS data as indicating a region of pronounced penetration underpins much of the reasoning in the paper, and if this interpretation is incorrect, then much of the further reasoning is also highly questionable.

3. Repository conditions

Based on the measured depth profiles, the authors estimate a bulk penetration rate due to diffusion of 1.3 μm/yr at 60 °C for S. This estimate is then used to linearly extrapolate the penetration depth and it is concluded that a 5 cm Cu canister wall would be penetrated in 38,000 years. We note again that we do not see the observed part of the depth profiles designated "pronounced penetration" as evidence of diffusion into the metal matrix. If, however, one were to assume that this region is indeed due to diffusion, then the following comment is of significance: Basic diffusion theory, see e.g., Section 2.4 in Ref. 4, implies that the bulk penetration depth increases as the square root of time, suggesting that 1 μm in one year corresponds to e.g., 1 mm in one million years, in stark contrast to the figure claimed in the paper.

The discussion on grain boundary diffusion is also confusing. Here the authors claim a penetration rate of 1.5 μm/yr at 60 °C for S and claim that this is compatible with the less than 1000 year theoretically calculated penetration time for 5 cm Cu reported in Ref. 4. However, also grain boundary diffusion depth varies slower than linearly with time [4]. Magnusson and Frisk [4] thus report that sulfur can diffuse 50 μm in less than one year at temperatures above 40 °C, i.e., considerably faster than reported in Ref. 1. It is also important to note that the data in Ref. 4 does not in any way discuss the extent of bulk or grain boundary diffusion, but merely the tentative time scales of the phenomena.

The authors claim that "in the presence of tensile strains, sulfide has been shown to cause stress corrosion cracking (SCC) of Cu in anaerobic chloride containing environments" and reference three studies in support of this claim. Here, we note that all these studies, and the one we are now commenting, have been carried out at conditions that are considerably more aggressive than those ever expected in for example a geologic repository at the intended Forsmark site in Sweden. This concerns both the concentrations of sulfide and the sulfide fluxes to the copper canister (where the latter depends on the diffusion of sulfide through the protecting bentonite buffer surrounding the canister and the

groundwater flux in fractures intersecting a deposition hole), which are both crucial for understanding the effects observed in the papers cited by Yue et al., see further Ref. 5. As pointed out in [5], there are alternative explanations than SCC also for observations made under such aggressive conditions. It is, furthermore, claimed that "these new findings provide reasonable explanations for the observations of sulfide-induced SCC and intergranular corrosion of Cu in similar environments". This conclusion is based on the claimed penetration rates of S, and, as elaborated above, we have serious concerns about the authors' measurements and discussion of penetration rates. We thus do not agree with the conclusion "Our new findings have important implications regarding the risk for sulfide-induced SCC and embrittlement of the Cu canister."

4. Conclusion

Yue et al. [1] claim to have observed penetration of corrosive species into copper exposed to simulated O_2-free groundwater. We have strong concerns about this interpretation of the ToF-SIMS data on which the claim is based. Interpreting the observed depth profile data as corrosion products rather than as penetration of species into the copper metal is compatible with findings in several other studies and in agreement with the general understanding of copper corrosion in sulfide solutions. We thus believe that the basic interpretation of the observations is erroneous, rendering the discussion in the paper confusing and misleading.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Fraser King reports a relationship with Swedish Nuclear Fuel and Waste Management Co that includes: consulting or advisory.

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