

Technical Report

TR-10-04

Stress corrosion cracking of copper canisters

Fraser King, Integrity Corrosion Consulting Limited

Roger Newman, University of Toronto

December 2010

Svensk Kärnbränslehantering AB

Swedish Nuclear Fuel
and Waste Management Co

Box 250, SE-101 24 Stockholm
Phone +46 8 459 84 00



Stress corrosion cracking of copper canisters

Fraser King, Integrity Corrosion Consulting Limited

Roger Newman, University of Toronto

December 2010

Keywords: SKBdoc 1227328, Stress corrosion cracking, Copper, Canisters, Lifetime prediction, Sulphide, Anaerobic conditions, Mechanism, Film rupture, Tarnish rupture, Film-induced cleavage, Surface mobility, Adsorption-induced dislocation emission, Crack-tip vacancy formation.

This report concerns a study which was conducted for SKB. The conclusions and viewpoints presented in the report are those of the authors. SKB may draw modified conclusions, based on additional literature sources and/or expert opinions.

A pdf version of this document can be downloaded from www.skb.se.

The following figures and text are reproduced with permission of the copyright holder:

Figures 2-1, 3-1 and 3-7 and quoted text in Appendix A with permission of Elsevier B.V., Amsterdam, The Netherlands.

Figures 2-2, 4-1, 4-2, 4-3, 4-4, and 4-5 with permission of the Nuclear Waste Management Organisation, Toronto, Canada.

Figure 3-2 with permission of NACE International, Houston, TX, USA.

Figure 3-3 with permission of ASM International, Materials Park, OH, USA.

Figures 3-5 and 3-6 with permission of Springer, Dordrecht, The Netherlands.

Abstract

A critical review is presented of the possibility of stress corrosion cracking (SCC) of copper canisters in a deep geological repository in the Fennoscandian Shield. Each of the four main mechanisms proposed for the SCC of pure copper are reviewed and the required conditions for cracking compared with the expected environmental and mechanical loading conditions within the repository. Other possible mechanisms are also considered, as are recent studies specifically directed towards the SCC of copper canisters.

The aim of the review is to determine if and when during the evolution of the repository environment copper canisters might be susceptible to SCC. Mechanisms that require a degree of oxidation or dissolution are only possible whilst oxidant is present in the repository and then only if other environmental and mechanical loading conditions are satisfied. These constraints are found to limit the period during which the canisters could be susceptible to cracking via film rupture (slip dissolution) or tarnish rupture mechanisms to the first few years after deposition of the canisters, at which time there will be insufficient SCC agent (ammonia, acetate, or nitrite) to support cracking. During the anaerobic phase, the supply of sulphide ions to the free surface will be transport limited by diffusion through the highly compacted bentonite. Therefore, no HS^- will enter the crack and cracking by either of these mechanisms during the long term anaerobic phase is not feasible.

Cracking via the film-induced cleavage mechanism requires a surface film of specific properties, most often associated with a nanoporous structure. Slow rates of dissolution characteristic of processes in the repository will tend to coarsen any nanoporous layer. Under some circumstances, a cuprous oxide film could support film-induced cleavage, but there is no evidence that this mechanism would operate in the presence of sulphide during the long-term anaerobic period because copper sulphide films appear to be insufficiently adherent.

A critical review of the surface mobility model is presented. It is argued that the formulation of the crack growth law is flawed and that, in its corrected form, predicted crack growth rates would be of the order of 10^{-20} m/s. Therefore, even if cracking were to occur via this mechanism, the crack velocity would be too small to lead to canister failure, even over repository timescales.

Two other SCC mechanisms, the adsorption-induced dislocation emission and vacancy injection and embrittlement models, are also discussed. Although these models are still in the development stage, it is considered unlikely that they could induce cracking during the long-term anaerobic phase.

Therefore, we conclude that the probability of SCC during the early aerobic period is low because of the absence of the necessary conditions for cracking and that there is no well-founded SCC mechanism that would result in cracking during the long-term anaerobic phase in the repository. Nevertheless, it is felt prudent to continue to study SCC of copper, especially under anaerobic conditions, in order to provide more support for the position that the stress corrosion cracking of copper canisters in the repository will not limit their service life.

Contents

1	Introduction	7
2	Review of the environmental conditions in the repository and factors leading to mechanical loading of the canister	9
3	SCC mechanisms and their relevance to copper canisters in a deep geologic repository	13
3.1	Film-rupture	13
3.2	Tarnish rupture	15
3.3	Film-induced cleavage	18
3.4	Surface mobility	22
3.5	Other mechanisms	28
3.6	Summary of mechanistic observations	29
4	Studies of the SCC of copper under repository conditions	31
5	SCC behaviour of copper canisters in a deep geologic repository	37
6	Conclusions	39
	References	41
Appendix A	Analysis of the published discussions of the Surface Mobility Model (SMM)	47
Appendix B	Surface mobility model as applied to SCC of copper and silver and their alloys in gaseous environments containing halogens	59

1 Introduction

The Swedish Nuclear Fuel and Waste Management Co (SKB) is investigating the disposal of spent nuclear fuel in a deep geologic repository in the granitic rock of the Fennoscandian Shield /SKB 2006/. A key component of the multibarrier system being developed is a corrosion-resistant copper canister that is expected to provide absolute containment for periods in excess of 100,000 years. Corrosion of the copper shell is one process that could limit the lifetime of the canisters, although a detailed review of possible corrosion processes indicates that long canister lifetimes are likely under the expected repository conditions /King et al. 2001, 2010/.

Copper is known to be susceptible to stress corrosion cracking (SCC) under certain conditions /King et al. 2001, 2010/. Of all of the corrosion processes to which the canister may be susceptible, SCC is one of the more difficult to assess since, at any reasonable crack growth rate, failure would occur within a relatively short period of time (compared with repository timescales). It is not practical, therefore, to make the canister sufficiently thick to avoid failure by SCC as would be the strategy in the case of general corrosion. Instead, it is necessary to demonstrate that either SCC will not occur or that, if it does, the period of crack growth is sufficiently short that a crack will not propagate through the canister wall within a short period of time.

In general, the probability of SCC can be reduced through sound engineering design /Jones 1992/, an approach that also applies to copper canisters in an underground nuclear waste repository in Sweden or Finland. First, the most obvious approach is to avoid choosing a material for a service environment in which it is known to be susceptible to SCC. Second, efforts can be made to reduce the tensile stress to which the object will be exposed, either through stress mitigation practices or through appropriate design. Third, the environment can be modified through the use of coatings or inhibitors, or through the use of agents that affect the electrochemical potential of the surface. These three approaches are clearly aligned with the common description of SCC as being the consequence of an aggressive environment acting on a susceptible material in the presence of a tensile stress.

Of these three prerequisites for SCC, that of particular importance for the disposal of nuclear waste is the nature of the environment. Over the long timescales of interest, the environmental conditions inevitably evolve /King et al. 2001, 2010/. For a backfilled repository located below the water table, as in the SKB and Posiva designs, for example, this evolution of environmental conditions can generally be characterised as a transition from a transitory early warm, aerobic phase to a long-term stable cool, anaerobic period. In corrosion terms, this evolution of the environment corresponds to a transition from relatively rapid and, possibly, localised corrosion behaviour initially, to an indefinite period of slow general corrosion. It has been argued that the SCC of copper canisters is unlikely to occur in the repository environment, and is only possible during the initial transient aerobic phase /King 1996, Maak and King 2005/.

This report is designed to complement the review of the SCC of copper canisters by /King et al. 2001, 2010/. Accordingly, this report is not an exhaustive review of the copper SCC literature, but instead focuses on the requirements for the four main mechanisms proposed and whether these prerequisites will be present in the repository. Since the majority of recent studies have focused on either the film-induced cleavage (Section 3.3) or surface mobility models (Section 3.4 and Appendices A and B), greater detail is provided for these two mechanisms than for the earlier film-rupture (Section 3.1) or tarnish-rupture models (Section 3.2). Because of the emphasis in this report on the SCC of copper canisters, the results of copper SCC studies performed under simulated repository conditions are also reviewed (Section 4). Based on this evidence, the expected SCC behaviour of copper canisters is discussed, with particular emphasis on how this behaviour changes with time as the environment evolves (Section 5). Of particular interest is whether SCC is only possible during the early aerobic transient phase, or whether SCC susceptibility continues into the long-term anaerobic period.

2 Review of the environmental conditions in the repository and factors leading to mechanical loading of the canister

Classically, SCC has been described as the consequence of the action of a suitably corrosive environment on a susceptible material in the presence of a tensile stress. Of these three factors, the two environmental-related factors (a suitable corrosive environment and the tensile stress) are discussed in this section. Issues related to the SCC-susceptibility of the canister material (oxygen-free copper with additional phosphorus (OFP copper)) are discussed for each mechanism in the next section, where appropriate.

The nature of the environment in the repository has been described in detail elsewhere /King et al. 2001, 2010/ and only the pertinent features are summarised here. In terms of the factors affecting the corrosiveness of the environment, the most important are the redox potential, the pore-water salinity and pH, temperature, and the generation of specific species that are known to support SCC. Those factors that affect the loading on the canister, and hence the level of possible tensile stress, are the hydrostatic head and bentonite swelling pressure and future glaciation events.

The most important characteristic of the repository environment is that it evolves over time. In general terms, the environment evolves from an initial warm, aerobic phase to an eventual cool, anaerobic condition that will resemble the undisturbed environment and which will persist indefinitely. This general evolution is illustrated schematically in Figure 2-1 /King et al. 2008/. It is expected that the duration of this aerobic-anaerobic transition will be of the order of 10's to 100's of years /Puigdomonech et al. 2001/, with the canister temperature dropping to ambient within a few 1000's of years /King et al. 2010/. In corrosion terms, this evolution of environmental conditions corresponds to a change from an early aggressive period, during which rapid general corrosion and possible localised corrosion are possible, to an ultimate benign period, during which only slow general corrosion is expected and which will be limited by the rate of transport of sulphide to the canister surface.

The shaded regions in Figure 2-1 represent the ranges of variability and uncertainty in the evolution of the environmental conditions within the repository. The rate of O₂ consumption will vary with location in the repository, both because the initial inventory will vary with the porosity and initial degree of saturation of the different sealing materials and because the rates of the different O₂ consumption reactions will vary. For example, in those sealing materials in which aerobic microbial respiration occurs, O₂ consumption could be very rapid (within a matter of weeks or months of repository closure). Similarly, the canister surface temperatures will vary spatially, partly because of the distribution in fuel burn-up and partly because canisters in the centre of the repository will tend to be warmer than those on the periphery.

Of primary importance among the environmental parameters is the redox potential and how it changes with time. The redox potential (E_h) is a measure of the relative oxidising and reducing power of the environment and establishes the maximum value of the corrosion potential (E_{CORR}) of the canister. The corrosion potential is a fundamental parameter in corrosion science and many forms of corrosion, including some types of SCC, occur only in certain ranges of potential.

In a Swedish/Finnish repository, the species that will determine the E_h (and, hence, partly determine E_{CORR}) are O₂, cupric species (Cu(II)), and sulphide ions (HS⁻). Oxygen will be trapped in the pores of the buffer and backfill material used to seal the deposition holes and tunnels. It is estimated that approximately 450 moles of O₂ will be present initially in the repository for each canister /King et al. 2010/, of which 95% will be in the tunnel and only 5% in the deposition hole. This O₂ will be consumed by a number of processes, including corrosion of carbon steel supports and other construction components, oxidation of Fe(II), HS⁻, and other oxidisable species, microbial activity, and by corrosion of the canister. In the latter case, O₂ is consumed by both the direct reduction on the canister surface and by the homogeneous oxidation of cuprous (Cu(I)) species to Cu(II). Copper(II) ions then become an oxidant for the corrosion of copper. Eventually, once all of the initially trapped O₂ and the subsequently formed Cu(II) ions have been consumed, the redox potential is likely to be dominated by reactions with sulphide species present either naturally in the groundwater because of

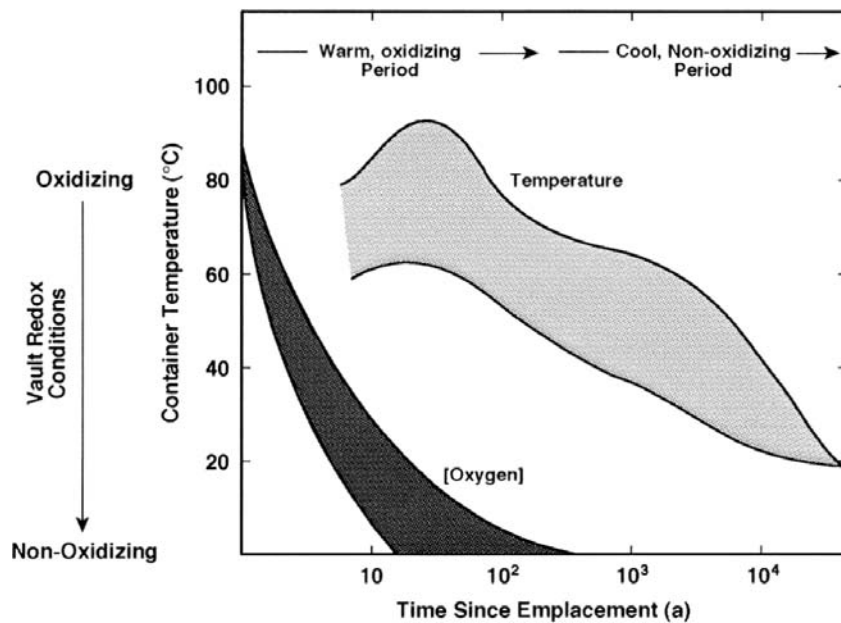


Figure 2-1. Schematic illustrating the evolution of environmental conditions within a deep geological repository /King et al. 2008/.

the dissolution of pyrite minerals or produced in the backfill or surrounding rock by sulphate-reducing bacteria /King et al. 2001, 2010, Masurat et al. 2010, Pedersen 2000/. Because of the strong complexation of Cu(I) by HS^- , copper is thermodynamically unstable in sulphide-containing water and the canister E_{CORR} will shift to significantly negative values. It is unclear whether there will be a period during this transition when Cu metal is in equilibrium with Cu(I) ions (e.g. as dissolved CuCl_2^-). For this to occur, the surface must be free of oxide (Cu_2O), which only occurs in acidic solution ($\text{pH} < 4$, /Pourbaix 1974/) and, therefore, seems unlikely in bentonite pore water buffered by the presence of carbonate minerals /King et al. 2001, 2010/. Equilibrium between Cu metal and Cu(I) ions may be important if such systems are shown to support SCC (see section 3.4).

The chemical composition of the pore water will depend on the composition of the groundwater at repository depth and on interactions with the bentonite sealing materials. Deep Fennoscandian Shield groundwaters tend to be saline, with chloride concentrations of several tenths molar possible at candidate repository sites in Sweden /King et al. 2001, 2010/. Table 2-1 summarises the likely ranges of composition of groundwaters in the Laxemar region near Oskarshamn and in the Forsmark-North Uppland area after resaturation of the repository /King et al. 2001, 2010/. The groundwaters are essentially Na/Ca-based chloride solutions, with a significant concentration of sulphate. The waters exhibit a slightly alkaline pH and are anoxic. Background levels of HS^- ions are low ($< 1 \text{ mg/L}$).

Ion exchange between the incoming groundwater and bentonite minerals and the dissolution of mineral impurities in the clay will modify the pore-water composition. The dissolution of calcite will effectively buffer the pore-water pH in the range pH 7–9 /King et al. 2001, 2010/. Furthermore, the exchange of Ca in the groundwater for Na in the clay will suppress the pore-water Ca content whilst leading to an increase in the Na concentration.

Other chemical species of interest are those that have been shown to support the SCC of copper, namely; nitrite, ammonia, and acetate ions. None of these species is present naturally in Swedish groundwaters, although ammonium ions are found at concentrations $< 1 \text{ mg/L}$ in Finnish waters /King et al. 2001, 2010/. The most likely route for the formation of these species is microbial activity /King 1996, Maak and King 2005/, although residues from explosives cannot be completely ruled out as an additional source. However, since microbial activity is suppressed in highly compacted bentonite, any such species will be formed predominantly by microbes active in the groundwater itself or in the tunnel backfill. Once formed, the ions must then diffuse to the canister surface through the bentonite /King and Kolar 2006/.

Table 2-1. Predicted chemical composition of the groundwater at repository depth in the Laxemar area in Oskarshamn and the Forsmark-North Uppland region after saturation of the repository. Concentrations are given in both mg/L and mol/L.

Constituent	Units	Laxemar	Forsmark-North Uppland
pH	–	7–8	7.1–8.7
Eh	mV	–180 to –250	–190 to –280
Na ⁺	mg/L mol/L	15–990 (0.7–43)·10 ^{–3}	90–3,750 (4–163)·10 ^{–3}
K ⁺	mg/L mol/L	2.6–29 (0.7–7)·10 ^{–4}	1–136 (0.3–35)·10 ^{–4}
Ca ²⁺	mg/L mol/L	40–960 (1–24)·10 ^{–3}	58–1,900 (1.4–47)·10 ^{–3}
Mg ²⁺	mg/L mol/L	4–90 (0.2–4)·10 ^{–3}	0.1–460 (0.01–19)·10 ^{–3}
Alkalinity	mg/L mol/L	60–150 (1.0–2.4)·10 ^{–3}	5–290 (0.1–4.8)·10 ^{–3}
Cl [–]	mg/L mol/L	11–2,910 (0.3–82)·10 ^{–3}	95–6,900 (2.7–194)·10 ^{–3}
SO ₄ ^{2–}	mg/L mol/L	7.5–210 (08–22)·10 ^{–4}	19–900 (0.2–9.4)·10 ^{–3}
HS [–]	mg/L mol/L	0.03–0.1 (0.9–3)·10 ^{–6}	0–0.30 0–10 ^{–5}

The other major “environmental” characteristic of importance is the development of a tensile stress (or strain) and the rate at which that stress changes. The sources of stress on the copper canister include:

- residual stress from the canister fabrication and closure weld procedures,
- bentonite swelling pressure of 8 MPa (range 5–13 MPa) /SKB 2006/,
- hydrostatic load of 4-5 MPa, plus an additional 22–26 MPa pressure during glaciation events /SKB 2006/.

The maximum applied load is, therefore, in the range of 31–44 MPa. Figure 2-2 shows, schematically the sequence of the application of these loads, but the precise timing depends on site and future climate variables.

Although the possible sources of residual and applied stress are understood, the prediction of the distribution of tensile stress on the canister surface, and how it varies with time, remains an area of uncertainty. Residual stress will be present on the copper shell following fabrication and sealing of the canister. Upon imposition of the bentonite swelling and hydrostatic pressures, the surface stresses become compressive on most parts of the canister but areas with tensile stresses will occur locally. Such areas are, for example, the regions close to the canister lid and bottom.

There is some doubt, therefore, whether the level of tensile stress on the canister surface will be sufficient to sustain SCC of the copper shell.

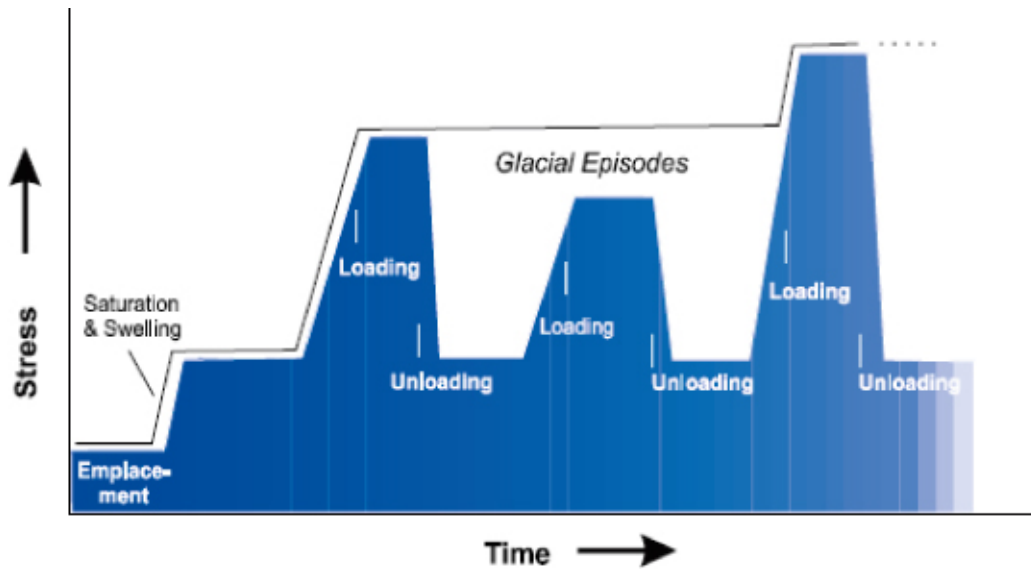


Figure 2-2. Schematic time dependence of the external loading of a copper canister due to hydrostatic loading and bentonite swelling pressures /McMurry et al. 2003/.

3 SCC mechanisms and their relevance to copper canisters in a deep geologic repository

In this section, the major mechanisms proposed for the SCC of copper are critically reviewed and their applicability to the cracking of copper canisters discussed. In determining whether a particular mechanism may result in the SCC of the canister, two factors are considered. First, whether the mechanism is valid and is supported by scientific evidence in the literature. Second, given that there is evidence in support of the mechanism, are the mechanistic requirements satisfied within the repository system, in terms of the necessary material, mechanical loading, and environmental considerations.

3.1 Film-rupture

Probably the longest-established SCC mechanism, the film-rupture mechanism, involves crack propagation following the rupture of some form of film at the crack tip (Figure 3-1) /Jones 1992/. Crack advance is typically believed to occur by a dissolution process, hence the synonyms of slip dissolution and slip oxidation /Jones 1992/, the latter often used when there is no clear evidence for dissolution at the crack tip. Anodic dissolution at the crack tip is supported by cathodic reactions on the crack walls or on surfaces outside the crack.

The crack velocity (v) is related to the anodic current density at the crack tip (i_{CT})

$$v = i_{CT} \frac{M}{zF\rho} \quad 3-1$$

where M is the atomic mass of Cu, z is the valency of dissolved metal, F is the Faraday constant, and ρ is the density of Cu. If the crack-tip strain rate ($\dot{\epsilon}_{CT}$) is slow, the crack tip periodically repassivates and the crack advances discontinuously at a rate given by

$$v = \frac{Q_F}{\epsilon_c} \dot{\epsilon}_{CT} \frac{M}{zF\rho} \quad 3-2$$

where Q_F is the charge density corresponding to crack advance and ϵ_c is the critical strain for film rupture.

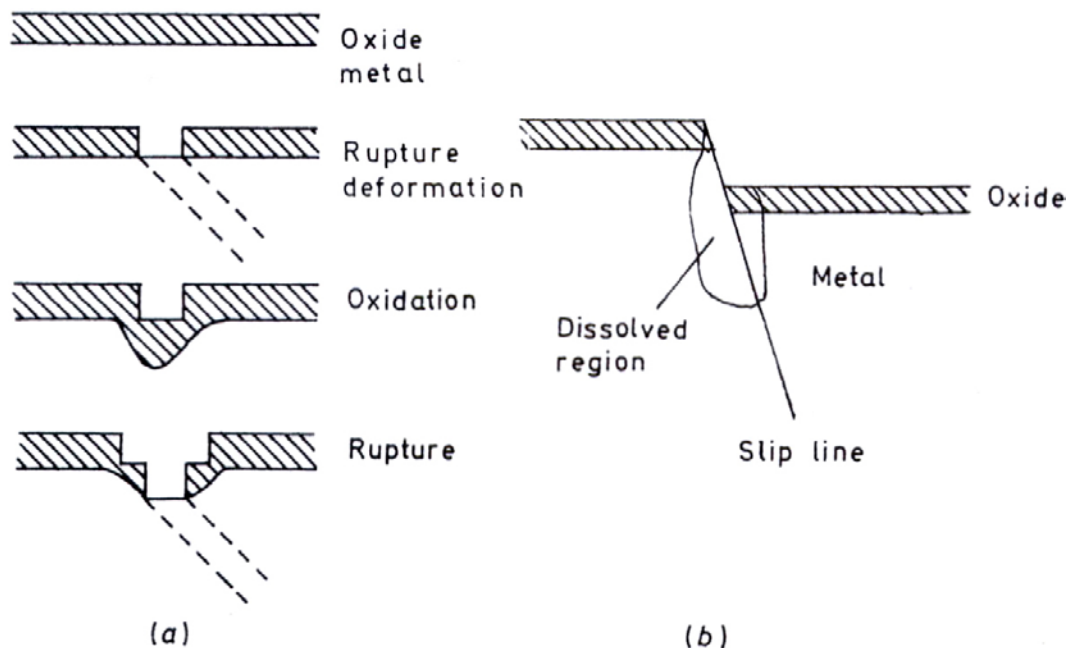


Figure 3-1. Schematic illustration of the film-rupture or slip dissolution model for stress corrosion cracking /Parkins 1976/.

A number of workers have proposed that the SCC of copper can be accounted for by the film-rupture mechanism, including:

1. /Uchida et al. 1991/, who reported the transgranular cracking of pure (>99.99%) copper in 1 mol/L nitrite solution at pH 7.3–7.5. Cracking was associated with the presence of a tarnish film, occurring at potentials near the $\text{Cu}_2\text{O}/\text{CuO}$ equilibrium line, and the authors could not rule out the possibility of a tarnish rupture mechanism.
2. /Pednekar et al. 1979/ observed transgranular cracking during slow strain rate testing (SSRT) in aerated 1 mol/L nitrite at the open circuit potential. Crack advance was attributed to dissolution following film rupture at slip planes.
3. /Benjamin et al. 1988/ studied the transgranular cracking of oxygen-free high-conductivity and of phosphorus-deoxidised copper in nitrite solutions (0.001–1 mol/L) at room temperature and at 80°C. There was evidence for a threshold potential and nitrite concentration, possibly associated with a crack-tip current density of $0.1 \text{ mA} \times \text{cm}^{-2}$. The two materials behaved identically.
4. /Yu and Parkins 1987/ reported transgranular SCC following initiation at grain boundaries in nitrite solutions of various concentrations at pH 9 and at various potentials. There was evidence for a threshold potential and nitrite concentration below which cracking did not occur. Fracture surfaces exhibited cleavage-like characteristics and crack arrest markings, and the authors were unable to discount the possibility of a film-induced cleavage mechanism.
5. /Thompson and Tracy 1949/ observed intergranular cracking in moist tarnishing ammonia atmospheres, which was attributed to dissolution following the rupture of a Cu_2O film.

The film-rupture mechanism has certain environmental requirements. First, conditions must be suitable for the formation of a protective film, most likely Cu_2O . Although this requirement is clearly met in solutions that result in a visible tarnish, a film may also be present at the crack tip in non-tarnishing solutions, such as those studied by Pugh and co-workers /Pugh 1979, Pugh et al. 1966/. Provided the pH inside the crack is not too acidic (<pH 4 at 25°C, Figure 3-2 /Pourbaix 1974/), a Cu_2O film would be present at potentials achieved in the presence of either O_2 or Cu(II) . Second, the environment must contain a species that will both support dissolution (so as to allow crack growth) and film formation (so as to maintain passivity of the crack walls and, if cracking is discontinuous, periodically passivate the crack tip). Although the formation of Cu_2O occurs in a wide range of solutions under appropriate conditions of potential and pH, the presence of ammonia has been found to be particularly adept at maintaining the necessary conditions at the crack tip. (The SCC of copper in nitrite solutions has been

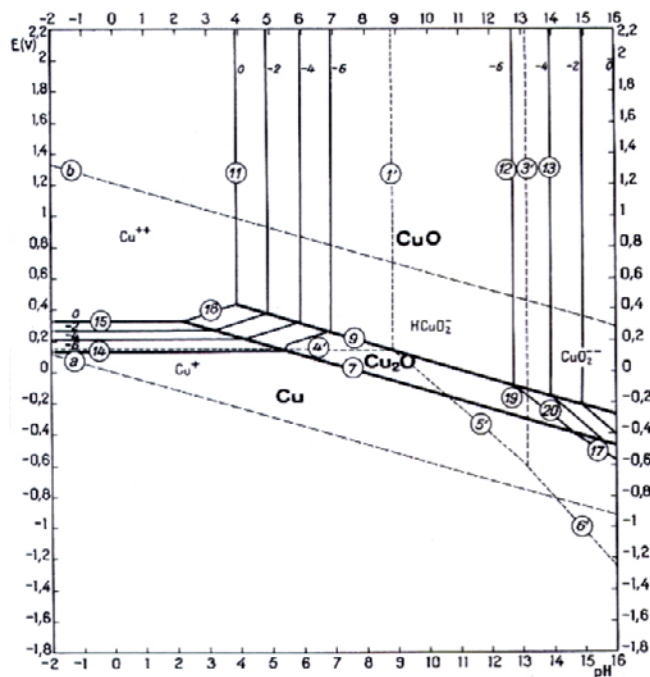


Figure 3-2. Potential-pH diagram for the $\text{Cu-H}_2\text{O}$ system with Cu_2O and CuO as the stable solid oxides /Pourbaix 1974/.

attributed to the formation of ammonia in the crack by the reduction of NO_2^- to NH_3 /Mori et al. 2005, Newman and Burstein 1980, Schwentenwein et al. 2002/). Third, there must be sufficient tensile strain to rupture the film at the crack tip. Straining of the copper shell will occur as the bentonite swelling pressure and/or hydrostatic head are developing and before the 1–2 mm gap between the shell and cast iron insert has closed. There is also the possibility of straining due to a shear load during glaciation events.

It is not evident that these three environmental requirements will be satisfied simultaneously within the repository. A Cu_2O film, or at least the conditions for film formation, will certainly exist early in the evolution of the repository environment, as will a period of straining of the copper shell (and, by inference, some degree of tensile deformation). However, based on predictions of the extent and location of microbial activity in the repository /King and Kolar 2006, King et al. 2001, 2010, Pedersen 2000/, it seems unlikely that microbial activity remote from the canister will result in sufficient, if any, nitrite or ammonium ions reaching the canister surface.

3.2 Tarnish rupture

The tarnish rupture mechanism is similar to the film rupture mechanism in that it involves a film (tarnish) and dissolution (Figure 3-3). The two mechanisms are distinguishable, however, on the basis that for the tarnish rupture mechanism crack advance occurs by fracture of the pre-formed tarnish, whereas in the film rupture mechanism crack advance occurs by dissolution following rupture of the film /King et al. 2001, 2010/. This may seem a subtle difference, but this distinction is maintained here as the two mechanisms have been historically considered separately.

The tarnish rupture mechanism has long been associated with the SCC of copper alloys because of the visible tarnish present on the surface of brass and copper in the so-called tarnishing ammonia solutions /King et al. 2001, 2010/. Because crack advance occurs by fracture of the pre-formed oxide, cracking is likely to be discontinuous in nature (since it would seem unlikely that the crack would arrest within the brittle oxide film rather than at the film/metal interface). The crack velocity is given by /King et al. 2001, 2010/

$$v = C \left(\frac{\dot{\epsilon}_{CT}}{\epsilon_C} \right)^{1/n} \quad 3-3$$

where C and n are constants describing the kinetics of tarnish growth, with $n = 2$ for parabolic kinetics and $n = 3$ for a cubic growth law.

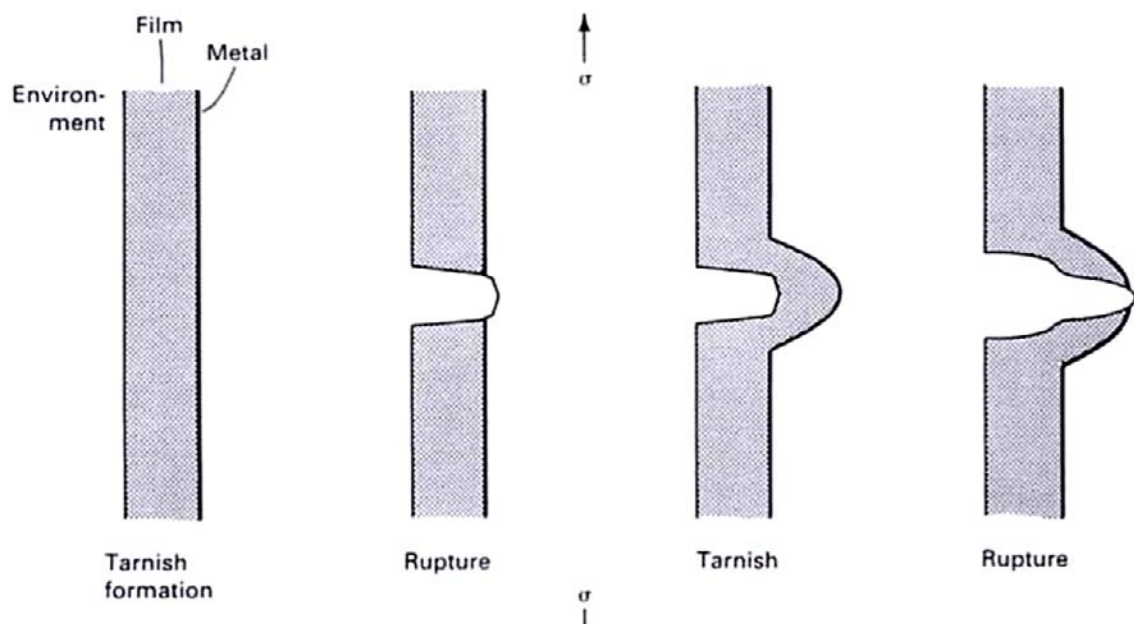


Figure 3-3. Schematic illustration of the tarnish-rupture mechanism for stress corrosion cracking /Jones 1992/.

Tarnish rupture has been proposed to account for the SCC of pure copper by the following authors:

1. /Uchida et al. 1991/ in 1 mol/L nitrite solution at pH 7.3–7.5. As noted above, the authors were unable to distinguish between film rupture and tarnish rupture mechanisms. Transgranular cracking was associated with the presence of a tarnish film, occurring at potentials near the $\text{Cu}_2\text{O}/\text{CuO}$ equilibrium line. It remains unclear, however, why rupture of the oxide would occur preferentially in the body of the grain, rather than at the grain boundary.
2. /Escalante and Kruger 1971/ in 0.025 mol/L cupric acetate solution. Intergranular cracking was believed to be the result of the cracking of a Cu_2O film.
3. /Suzuki and Hisamatsu 1981/ in dilute (0.05 mol/L) ammonia solution. Transgranular cracking of pure (99.999%) copper occurred under conditions where an adherent Cu_2O film formed, but not at higher ammonia concentrations where the film was only poorly adherent. As noted above, for tarnish rupture to explain transgranular cracking, there must be some mechanism by which the oxide grows preferentially, or is more-easily fractured, in the body of the grain rather than at the grain boundary.

The environmental requirements for the tarnish rupture mechanism are similar to those for film rupture. A film or tarnish must clearly be present and has been associated in the literature with the formation of Cu_2O in ammonia, nitrite, or acetate solutions. Such a film is present under a wide range of pH conditions in aqueous solutions (Figure 3-2). Cuprous oxide will be stable during the aerobic period in water (Figure 3-2) and dilute Cl^- solutions (Figure 3-4), but becomes increasingly soluble with increasing $[\text{Cl}^-]$, requiring a higher pH to stabilise the film. Cuprous oxide is only thermodynamically stable for potentials more positive than the $\text{Cu}/\text{Cu}_2\text{O}$ equilibrium line. Theoretically, no oxide film will be present in O_2 -free water, but the kinetics of oxide dissolution will determine at what stage the surface becomes free of oxide as the repository redox conditions become more anaerobic.

In the repository, therefore, the surface will only be covered by an oxide for a limited period of time, starting initially and ending at some stage after the consumption of all of the oxidant (O_2 and Cu(II)). Dissolution of the oxide and the development of a film-free surface will be promoted by increasing salinity of the bentonite pore water as the repository saturates with groundwater.

There is some question about whether a Cu_2S film could play the same role as Cu_2O in promoting SCC via a tarnish rupture (or, indeed, film rupture) mechanism. There are analogies to the system copper-water-sulphur in other metal-environment systems that make it difficult to exclude the possibility of SCC. For example, SCC of copper occurs in slow strain rate testing in gaseous halogens, as discussed later on in the context of the surface mobility model, and there is no evidence that Cu(I) halide formation under those conditions is especially rapid compared with the rates reported for sulphidation of copper in mM-strength sulphide solutions /Smith 2007/. However there is no information on such cracking under static loading – one can anticipate greater difficulty of SCC in a pure metal under static loading than in an alloy, where there is always the possibility of some selectivity of oxidation and the slip characteristics are often more favourable for SCC (coarse rather than fine slip). Moreover, sulphidation of copper does not always produce a well-adhered or protective film. Once a small crack is present, the continuing reaction on the walls and external surface exacerbates the diffusion limitation for sulphide reaching the tip. In principle, crack propagation in such a situation is impossible if the free-surface reaction is already under sulphide diffusion control, since no sulphide can reach the crack tip. Finally, since sulphidation of copper involves little or no dissolution – at least in highly diluted solutions – and involves a volume expansion, this is not a favourable situation for SCC under static loading from residual stress. There will always be a compression induced by the intergranular sulphidation that will tend to counteract the externally applied stress. Some might argue that instead there will be a wedging effect – this requires that the crack walls continue to sulphidise and press against each other. But in one well-studied case where such a ‘tarnishing’ mechanism of SCC occurs – the so-called SICC or **strain-induced corrosion cracking** of steel in hot water, the induced compression effect from the iron oxide film strongly hinders cracking, unless there is an applied dynamic tensile strain /Heldt and Siefert 2000/.

Ongoing work at the University of Toronto is examining the selectivity, if any, of copper sulphidation to grain boundaries and deformation features. Again, even such subtle penetration into the material will be hindered if the sulphidation reaction is under aqueous-phase diffusion control. According to /Smith 2007/, the films are in a critically stressed state, such that in identical experiments – especially under free-corrosion conditions – one may obtain either a relatively protective or

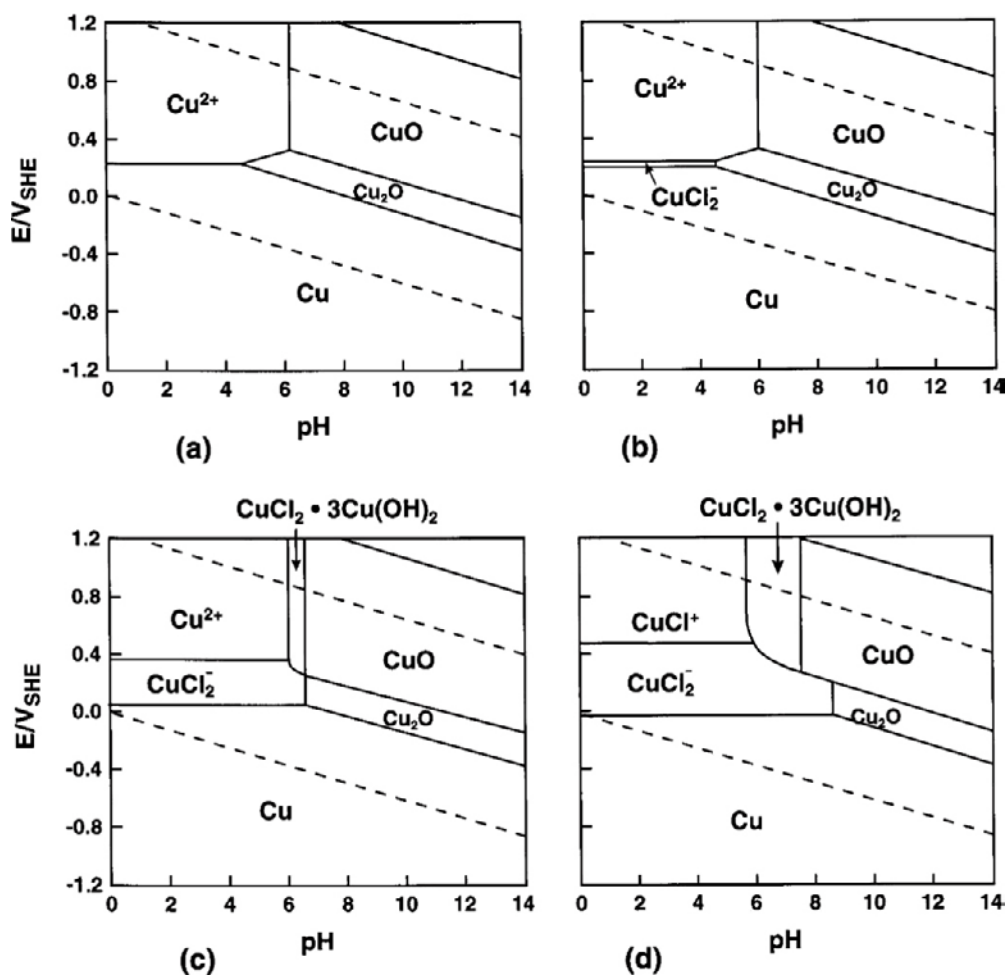


Figure 3-4. Potential-pH diagram for the Cu-Cl-H₂O system with Cu₂O and CuO as the stable solid oxides /King et al. 2001, 2010/. Figures are shown for Cl⁻ concentrations of (a) 0.001 mol/L, (b) 0.01 mol/L (c) 0.1 mol/L, and (d) 1 mol/L. Equilibria between solid and dissolved species (solid lines) shown for a total copper activity of 10⁻⁶ mol/L. The upper and lower dashed lines represent the stability field of water and denote the evolution of O₂ and of H₂, respectively.

a completely unprotective film. The protective type of film is more dangerous, because it removes the mass transport limitation for the free surface and crack wall, focusing the attack on the crack tip.

Phosphorus segregation to grain boundaries may exacerbate any tendency for sulphidation to localise and create cracks or intergranular fissures. Not much seems to be known about this possibility. Since phosphorus reacts with water spontaneously, this also represents a remote possibility for SCC in anaerobic conditions without sulphide, although the grain-boundary coverage of phosphorus is probably not high enough for such a mechanism to operate. One can imagine that P would have to somehow form a percolating network in the boundaries, and even then the kinetics would be slow because the copper is not reacting and the resulting fissure is unreasonably narrow.

The recent report of sulphide-induced SCC of copper in slow strain rate tests /Taniguchi and Kawasaki 2008/ is not surprising. SCC occurred under very severe mechanical conditions and in relatively strong sulphide solutions (>0.005 mol/L). The cracks appear to have formed near the end of the tests; similar cracking could probably have been produced in many different environments. The key is the ability of such cracks to continue growing under static loading after having been initiated by slow straining. Perhaps the Taniguchi cracking is really just an example of "SICC". In fact, even the well-known SCC of copper in nitrite solution is very dependent on dynamic straining, as shown by /Sieradzki et al. 1984/. But perhaps "SICC" is mainly a phenomenon that occurs when cracks are trying to grow transgranularly, and intergranular SCC is more facile in the long term – such considerations are at the limit of present understanding of SCC.

3.3 Film-induced cleavage

The film-induced cleavage model of SCC /Sieradzki and Newman 1985, 1987/ arose from a prior history that began with the work of Edeleanu and Forty around 1960 /Edeleanu and Forty 1960/, and continued with the work of E.N. Pugh and others on cleavage-like transgranular SCC (T-SCC) /Beavers and Pugh 1980, Pugh 1985/. All these authors believed that T-SCC, occurring under strongly anodic conditions or in noble-metal alloys (including brass) could not be due to purely anodic processes, but must involve periodic brittle fracture of the substrate. Initially both Edeleanu and Forty and Pugh believed that some kind of bulk embrittlement was involved (Figure 3-5), with short-range order and hydrogen absorption being suggested as causal factors. But eventually the view solidified that each small cleavage event must be triggered by a thin surface layer with special mechanical properties. De-alloying and its associated nanoporosity became the focus of further research into how such “cleavage” (or brittle intergranular fracture) of fcc metals was possible, since the most spectacular examples of T-SCC were in systems (brass, austenitic stainless steel, Cu-Au) where a correlation of SCC with de-alloying could be demonstrated or at least postulated /Barnes et al. 2008, Kelly et al. 1991, 1993, Newman 2002, Newman and Saito 1993, Newman and Sieradzki 1987, Saito et al. 1993, Shahrabi and Newman 1989, Shahrabi et al. 1993, Sieradzki et al. 1987/. It was recognised, of course, that T-SCC of pure copper in nitrite solution could not be due to de-alloying, and in the paper that showed the first detailed fractographic study of this phenomenon /Sieradzki et al. 1984/ it was suggested that an oxide with special mechanical properties might be responsible (Figure 3-6). This was not a particularly satisfactory suggestion, and later on /Sieradzki and Kim 1992/, working with pure copper in an acetate solution, referred to porosity, analogous to that formed by de-alloying, even in this pure-metal system.

The use of the term ‘cleavage’ reflects a view, or prejudice, drawn from Pugh’s work on brass. Pugh thought that intergranular SCC was a continuous, “bond-by-bond” process, and that only T-SCC involved the brittle type of fracture. This might be true for brass, but in gold alloys the most spectacular film-induced fracture is intergranular /Kelly et al. 1991, Saito et al. 1993/, although cleavage can be obtained under certain conditions or in monocrystals /Barnes et al. 2008/ (Figure 3-7).

The work of Aaltonen and others on internal friction /Aaltonen et al. 1998, Jagodzinski et al. 2000/ is relevant here, since whatever one may think is the origin of their Hasiguti peaks¹ after oxidation of copper in nitrite solution, there is clearly some special surface process that occurs in the potential range where SCC is observed.

Not all authors agree with the prime role placed on de-alloying (or other means of generating a brittle surface layer). According to /Flanagan et al. 1993/, any kind of corrosion, not necessarily involving a surface film, can generate microcleavage. Their model is interesting and very general, but their views may have been unduly influenced by the supposed observation of SCC of CuAu alloys below the critical potential for de-alloying, a result we now know to be incorrect /Newman and Senior 2010/.

T-SCC of copper is possible in some other environments when the copper is highly cold worked /Shirai et al. 1982/².

¹ Peaks in internal friction due to thermal unpinning of dislocations from point defects; in the case of the Aaltonen work, the latter are proposed to be vacancies injected by corrosion.

² In 1987, Roger Newman was asked to serve as an expert witness in a legal case, in which hard-drawn, mainly stranded overhead copper conductor wires had failed in a rail tunnel. The fractures resembled fatigue, but the necessary cyclic stress was hard to identify. Colleagues located quite an extensive Japanese literature that had followed a series of similar failures on the Shinkansen or high-speed rail network in Japan. In that particular case the problem was solved by removing plastic sheathing that had allowed polluted rainwater to collect on the wires. The cracking could well have been due to ammonia in practice, but in lab testing it was shown that prolonged immersion of bent conductor samples in dilute sulphuric acid would lead to T-SCC. As recalled 20 years later, the protocols that were followed were not particularly rigid, and it cannot be excluded that the pH increased (by corrosion) until a Cu₂O film could be formed, which occurs at or above ca. pH 3 in CuSO₄ solution. Nevertheless, this type of cracking is interesting, since it involves no complexants and (potentially at least) no surface film, yet T-SCC occurred. Whether or not this phenomenon was due to film-induced cleavage is unclear.

One thing we can be sure of is that film-induced cleavage of copper cannot occur under anaerobic conditions. It also appears unlikely in a reducing but sulphide-containing system, since a sulphide film is poorly adherent and thus not a particularly suitable nucleating layer for cleavage.

Films other than oxides or de-alloyed layers have been implicated in T-SCC propagation. The T-SCC of carbon steel in anhydrous ammonia or anhydrous ammonia-methanol solutions occurs under relatively mild conditions and is clearly not due to hydrogen; it was suggested /Newman et al. 1992, Procter et al. 1992/ that a thin nitrated layer was responsible for periodic cleavage nucleation. The role of oxygen in such cracking would then be to provide the necessary oxidising potential so that ammonia can be oxidised to nitrogen atoms. There does not appear to be any analogous interstitial embrittlement that could operate in copper.

Cracking analogous to film-induced cleavage can be obtained by ultra-high strain-rate deformation of copper; microcracks initiate at the bottom of dimples on the fracture surface, near second-phase particles /Petit and Dequiedt 2006, Zurek 1987/. However, the necessary high strain rate would not occur on a canister in the repository.

In so far as film-induced cleavage involves nanoporous metallic layers, it is an inherently rather rapid cracking mechanism. Open nanoporosity in a metal such as copper (which does not have a particularly high melting point) is unstable and will coarsen by surface self-diffusion. Such coarsening destroys the ability of the nanoporous layer to inject a crack. As a result, cracking tends to occur rapidly, or not at all. Oxides have a high melting point and the surface mobility is low, so the ‘self-annealing’ effect seen with the nanoporous metal is less likely. However, we have no data one way or the other (apart from the empirical observation of SCC in nitrite) to suggest whether film-induced cleavage involving an oxide film could be a slow, long-term SCC mechanism. Generally the belief of those working in this field is that there is something exceptional about nanoporous metals with regard to crack injection, and recent advances in the understanding of the extraordinary mechanics of de-alloyed materials (near-theoretical strength in compression, for example) tend to confirm this view /Weismüller et al. 2009/.

Kinetic formulation of the film-induced cleavage model

Here we consider cleavage (or brittle intergranular crack) nucleation by a nanoporous metallic layer, but certain oxides could equally well suffice; however these do not induce tension (as the nanoporous metal does by its thermodynamic tendency to shrink by surface diffusion), so they will not be associated with easy, well-known cases of SCC.

The simplest case is just a refinement of the slip-dissolution or film-rupture model that nowadays is mostly associated with Ford and Andresen /Andersen and Ford 1988/ and Shoji /Lu and Shoji 2006/. In that model we write the crack velocity v as:

$$v = \int_0^{\tau} i(t) dt \cdot \left(\frac{A}{zF\rho\tau} \right) \quad 3-4$$

with

$$\tau = \frac{\epsilon_f}{\dot{\epsilon}_c} \quad 3-5$$

where $i(t)$ is the anodic current density transient on the bare metal surface at the crack tip, A is the atomic weight of the metal and ρ its density, z is the number of electrons transferred per atom dissolved, and t is the interval between film rupture events which is the fracture strain of the film, ϵ_f , divided by the crack-tip strain rate, $\dot{\epsilon}_c$.

Let us assume (a) that all the anodic charge goes into the formation of a nanoporous metal layer of thickness h ; and (b) that there is a critical nanoporous film thickness h^* that is required for cleavage nucleation. To get the layer thickness from the current density transient we need a correction factor a ; this recognizes that we are not oxidizing all the metal when we create the layer.

Thus for a depth of chemical attack, L , on each film rupture event, where

$$L = \int_0^{\tau} i(t) dt \cdot \left(\frac{\alpha A}{zF\rho} \right) \quad 3-6$$

that is less than h^* , we revert to slip-dissolution or ‘film rupture’ but with the film being the nanoporous metal.

But for $L > h^*$, we suppose that the crack jumps ahead a distance H by purely mechanical fracture. If $H \gg L$, the crack velocity is simply

$$v = \frac{H}{\tau} \quad 3-7$$

The first refinement, in line with the experimental observations of /Edeleanu and Forty 1960/ and /Beavers and Pugh 1980/, is to note that the crack jumps further, though much less often, at lower stresses. This could be an effect of stress, but it is more likely to be an effect of greater layer thickness at the moment of the crack jump. So, for $h > h^*$,

$$H = H(h) \quad 3-8$$

and

$$v = \frac{H(h)}{\tau} \quad 3-9$$

Rather than postulating a critical layer thickness h^* , we could also consider that H is a continuous function of h even at small h – this is more convenient mathematically, but we do not know what the function is.

A second, very difficult, refinement, is to include the induced elastic stress and strain (effectively, a contribution to $\dot{\epsilon}_c$) from the layer formation. Generally this will be tensile for a de-alloyed layer and compressive for an oxide. We do not know how to do this, but experiments using foil bending to measure the stress are possible. Essentially, for a dealloying system the crack tip strain rate due to creep, or to the crack extension itself, becomes less important, and cracking becomes easier under static loading; conversely cracking becomes more difficult for an oxide system as postulated for copper.

An important, but again very difficult, modification would address the ageing of the surface layer. Nanoporous metallic layers age by surface diffusion and lose their ability to nucleate brittle cracking. Generally, the kinetics of ageing, expressed as pore or ligament size l as a function of time, are of the form:

$$l \sim t^{1/4} \quad 3-10$$

as for any process dominated by interfacial diffusion. If we postulate a critical ligament size l^* above which crack injection cannot occur, then we can see that with time, the layer will develop an inner part that might inject a crack (depending on crack-tip strain rate etc.), and an outer, coarsened part that plays no role in crack injection. For de-alloyed layers, the layer growth kinetics are rather linear, or at worst parabolic. On the assumption that they are linear, then the rate constant for the coarsening of the porosity, k_c , which is related to the surface self-diffusivity of the metal, and the rate constant for the layer growth, k_g , jointly determine how much of the layer is available for crack nucleation at any moment.

It is impossible to make further progress on the possibility of film-induced cleavage (FIC) in pure copper without straying into speculation, but the main conclusions are

- FIC is highly unlikely from a sulfide film of the type usually discussed.
- FIC has been postulated to occur in copper during anodic dissolution at the crack tip, but this is a specialized case and not pertinent to SKB’s concerns.
- A kinetic formulation of FIC is possible but has a number of unknown parameters.

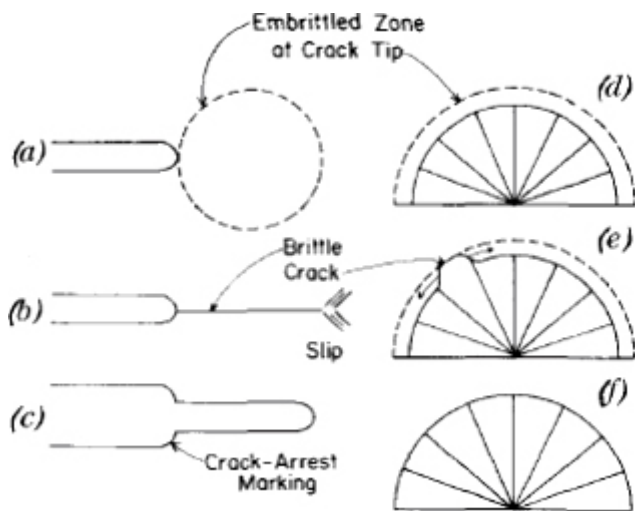


Figure 3-5. Schematic of T-SCC crack propagation in brass by /Beavers and Pugh 1980/, published at the time when Pugh still believed that some form of bulk embrittlement was responsible for the brittle microcracking. Nowadays we would draw a similar diagram, but with a brittle film coating the crack.

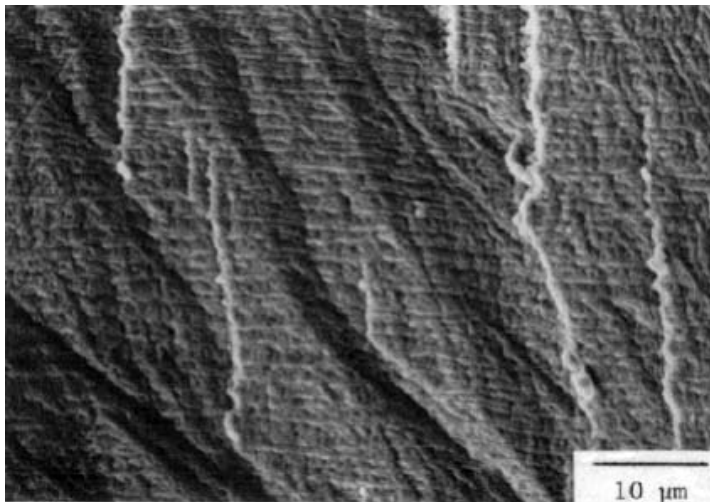


Figure 3-6. Striated fracture surface of copper after slow strain rate testing in sodium nitrite solution /Sieradzki et al. 1984/, suggesting a discontinuous, brittle mode of crack growth (crack growth top to bottom).

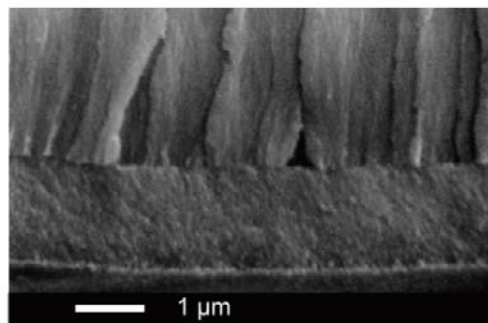
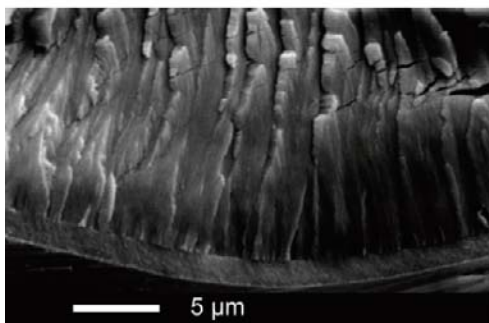
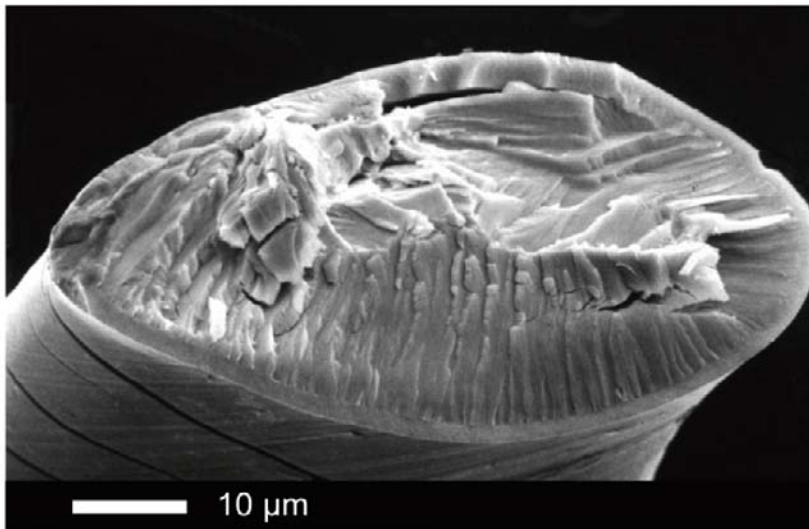


Figure 3-7. Film-induced cleavage of Ag-23 at.% Au after de-alloying in aqueous perchloric acid /Barnes et al. 2008/.

3.4 Surface mobility

The model and criticisms of its scientific basis

This model was introduced by Galvele in 1987, and occasionally updated or applied to particular topics such as nuclear materials /Galvele 1987, 1993, 1996, 2000/. It postulates that a crack tip under stress captures vacancies, not from the bulk of the material but from the surface – or to put it another way, surface self-diffusion of metal atoms away from the crack tip grows the crack (Figure 3-8). Obviously there are similarities between such a process and creep crack growth. The questions are whether the model is correctly constructed and whether it uses the right stress? Are the parameters in the model reasonable?

According to Galvele, the crack propagation rate (cpr) is given by:

$$cpr = \frac{D_s}{L} \left[\exp \left(\frac{\sigma \cdot a^3}{kT} \right) - 1 \right] \quad 3-11$$

where D_s is the applicable surface (self) diffusivity, L is a diffusion length along the crack flank (Galvele always uses 10^{-8} m for this), s is the opening stress at the crack tip and a is the atomic size (approximate volume of a vacancy).

One can argue about the assumption of an extremely sharp crack that is inherent to the model, or about capillary effects that would tend to close up such a crack, or about the value of stress that has to be used to fit the data, but the main controversy concerns the basic energetics of the calculation. Since the reduction in vacancy formation energy due to tensile stress (sa^3) is in the argument of an exponential, the model could be extremely vulnerable to any error in the formulation of this quantity. According to /Sieradzki and Friedersdorf 1994/ there is an elementary error: sa^3 is only appropriate, as originally formulated by /Nabarro 1948/ and /Herring 1950/, for the **interior of the solid**. Sieradzki recently summarised his argument as follows (private communication):

“In his formulation for the vacancy concentration at the crack tip the argument of the exponential is a stress (at the crack tip) \times atomic volume/ kT . Since the crack is a free surface the energy term should be $(\text{stress})^2 \times \text{atomic volume}$ divided by $2EkT$ where E is Young’s modulus. The difference [between the proposed formulation and that for a free surface] in the vacancy concentration then is a factor of $\text{stress}/2E$, in the argument of an exponential!”

As early as 1993 (but in a paper inaccessible to Sieradzki and Friedersdorf), Galvele clarified that he was actually assuming that the sink for the vacancies was **ahead** of the crack (see Appendix A). This appears at first sight to destroy the surface mobility model, or turn it into a vacancy injection model where surface diffusion is not the rate determining step, but Galvele got around this difficulty by assuming that SCC cracks are atomically sharp, so that the diffusion in the solid lattice might only have to proceed for a few atom spacings. This conflicts with most continuum mechanics solutions for cracks in metals, whether moving or static.

The remainder of this discussion assumes, for the sake of argument, that this apparently fatal flaw might be overcome. /Sieradzki and Friedersdorf 1994/ assumed (having only read the 1987 Galvele paper) that he was talking about a stress acting parallel to the crack-tip surface. Indeed, in that case, their assumption of equilibrium vacancy concentration on the crack flank might be erroneous, as this is generally a corroding or at least a dynamic interface.

This issue of the energetics of a Galvele type of model is not closed. The science of crack-tip mechanics and geometry, for moving cracks, is still under development. The stress corrosion community, under the leadership of R.W. Staehle, has recently started to debate the question – “why are SCC cracks so sharp?” /EPRI 2007/. If we do not understand that, it seems possible that we do not understand what energy term, exactly, should go into the crack propagation rate equation – or, possibly, the actual stress at a crack tip may be closer to $E/50$ than $E/500$, so that the error is not as large as Sieradzki indicates. In fact, for most conditions of interest to us, the exponential is nearly linearised, so the factor by which Galvele overestimates the crack velocity is only $2E/s$ which is a few thousand at most (neglecting the serious capillary-closure problem for tight cracks that is also identified by Sieradzki). In Appendix A we analyse Galvele’s responses (we believe, not entirely adequate) on this issue.

When /Sieradzki and Friedersdorf 1994/ take into account the capillary effect and work with chemical potentials instead of concentrations, they obtain the following equation:

$$V_n \cong \frac{D_s N_s \Omega^2}{kT} \frac{2}{\pi} \frac{1}{\rho^2} \left(\frac{\sigma_{yy}^2}{2E} - \gamma\kappa \right) \quad 3-12$$

where V_n is crack velocity, N_s the number of atoms per unit area of surface, Ω is the volume of a vacancy (the same as a^3), ρ is the crack-tip radius and κ is the corresponding curvature ($1/\rho$); γ is the surface energy. Clearly the crack closes up by capillary action if the term in the brackets becomes negative, and when it is positive there is a (large) value of r for which the velocity is maximised. γ is around 1.5 J/m^2 for bare metal in electrolyte. Sieradzki obtains very low crack velocities with this approach, and of course it points out a fundamental problem with Galvele’s treatment, that he *needs* very sharp cracks for his model to work, but such cracks are unstable.

Whilst it is true that the Galvele model is a kind of creep model, the fact that it applies to the crack-tip and nearby surfaces, rather than occurring in the bulk of the material, creates distinctive features. Neither is nucleation discussed in the Galvele model, as it is – extensively – in the creep literature. One can point to well known papers on creep cavity nucleation and growth /Davanas and Solomon 1990, Raj 1978/ and postulate a relation between the grain-boundary transport of atoms in such models and the surface transport postulated by Galvele (the former is much slower of course), but such analogies are not exact, neither is the stress state the same. Importantly, though, such models do contain capillarity, and as a result sharp cracks cannot exist – something that Sieradzki considers a major flaw in Galvele’s treatment. Of course there is no analogy in such models to transgranular SCC.

In our further discussion we shall assume, just for ultimate conservatism, that the capillary argument can be circumvented somehow, so that we just need to correct equation 3-11 by using the right expression for the vacancy formation energy.

Surface diffusivities

Clearly the surface mobility model, since it relies on a kind of creep, does not require an oxidising environment, or any environment at all. But since D_s values are relatively low for bare engineering metals, Galvele relies on contamination of the surface to increase D_s , citing the ultra-high vacuum (UHV) studies of Rhead on copper surfaces contaminated with halogens /Delamare and Rhead 1971/ (incidentally Rhead worked nowhere near room temperature – the lowest temperature for which he gives data for clean copper is 700°C; he shows data down to 400°C for halogen-contaminated surfaces). Since the advent of the STM and AFM, there is a huge amount of new information on surface diffusion, including studies performed *in situ* in electrolytes /Baier et al. 2002, Doña and Gonzalez-Velasco 1992, Giesen 2001, Martins et al. 1996, Trevor and Chidsey 1991, Vasiljevic et al. 2006/. Amongst other things, this literature shows that the surface diffusion *mechanism*, as well as the rate, changes as we vary the metal, crystal orientation, environment or potential. For example, on copper the adsorption of chloride actually hinders diffusion of adatoms across terraces /Baier et al. 2002/ (Rhead refers to this as ‘skating’, where metal atoms diffuse on top of an adlayer of Cl or CuCl), but dramatically enhances the mobility of step edges.

The D_s value becomes something of an adjustable parameter in many publications on surface mobility, but there does seem to be a correlation between D_s and cpr , even though some of the assignments are a little contrived. Generally, Galvele estimates D_s from the melting point of the surface compound that is assumed to be present at the crack tip, using an established correlation. If one takes the relevance of Rhead’s work at face value, this is reasonable for gaseous systems with low pressures of halogen, but it is hard to interpret such a procedure where there is massive 3D compound formation. In that case one has to imagine metal atoms diffusing along an interface between the compound and the metal.

So far, the Galvele group seems to have overlooked an observation that might help the feasibility of the surface mobility concept – that D_s values can be higher by orders of magnitude in electrolytes than in vacuum, even for a noble metal (gold) in perchlorate solution where there is no specific adsorption of anions. /Dursun et al. 2003/ report a value for D_s (Au) of 2×10^{-16} cm²/s in plain aqueous perchloric acid at ambient temperature, increasing to 8×10^{-13} cm²/s in the presence of iodide ions (both these values were for dealloyed AgAu alloys, so not strictly for pure Au). Even higher values were reported by /Doña and Gonzalez-Velasco 1992/ for smoothing of roughened gold in perchloric acid: 3×10^{-15} to 2×10^{-13} cm²/s. Much lower values are obtained in dry experiments /Porath et al. 1995/. However, it is not so evident that this electrolyte enhancement occurs on copper. /Martins et al. 1996/ quote 7×10^{-17} cm²/s for copper in sulphuric acid containing copper ions (this was a rather complicated experiment carried out on a platinum electrode, and distinguishing between the anodic stripping behaviour of Cu atoms bound to Cu and Cu bound to Pt). On the other hand, one Rhead publication /Barthes and Rhead 1978/ gives D_s for Cu in vacuum at room temperature as 10^{-15} cm²/s. Even higher values have been reported or can be extrapolated, such as 7×10^{-15} cm²/s

/Gontier-Moya et al. 2004/.³ With an activation energy of ca. 72 kJ/mol, and given that nuclear waste canisters are warm – say 350 K – the most conservative approach would dictate using a vacuum value of D_s of about 3.5×10^{-13} cm²/s. The corresponding value for electrolyte, from Martins, and assuming the same activation energy, would be 3.5×10^{-15} cm²/s.

³The value of D_s changes markedly when there is any oxidation of the metal, even monolayer oxidation or OH electroadsorption. On metals such as gold, this is manifested as a reduction in D_s occurring above a particular, relatively oxidising potential, and it is easy to make D_s estimations below this potential and to show that D_s is enhanced by the electrolyte. For copper, however, the formation potential of CuOH_{ads} is very negative, so much so that CuOH can form by reaction of a copper surface with water /LaGraff and Gewirth 1995/. In that situation, it is not self-evident that the usual enhancement of D_s by electrolyte will occur – there could even be a reduction. Incidentally, reaction of copper with water to produce hydrogen has been proposed to be a continuing process that can lead to long-term corrosion in an anaerobic waste repository (without sulphide) /Szakálos et al. 2007/, but the only way we can see any hydrogen being produced is if the monolayer oxidation of copper somehow masquerades as a bulk corrosion process. This can happen if the copper is available as very small nanoparticles, so one could postulate that initial aerobic corrosion followed by oxygen consumption and disproportionation of Cu(I) produces such particles in high yield; they subsequently corrode to ‘CuOH’ (the adsorbed, 2D version) until suitable sites are used up. This is not a continuing, long-term corrosion process that should cause any concern, although it certainly deserves attention.

Effect of strain rate on crack velocity in slow strain rate tests

According to Galvele, the effect of strain rate on crack velocity in slow strain rate tests is entirely due to variation in the stress at the tip of the crack; none of the other quantities in equation 3-11 are considered to vary with strain rate. Therefore, since some systems show a 2 or 3 orders of magnitude increase in crack velocity over the applicable range of strain rates /Serebrinsky and Galvele 2004, Serebrinsky et al. 1999/, there has to be a corresponding increase in stress. Since the argument of the exponential is small, even for large stresses, the exponential is close to linear, and a large variation in crack-tip stress is required over the studied range of strain rates – not 3 orders of magnitude, but much larger than is normally thought to exist according to elastic-plastic fracture mechanics.

Passive systems

For systems showing simple passive-film (oxide) formation, Galvele rationalises the absence of SCC by quoting evidence for growth of such films by inward anion (oxygen) migration – thus no vacancies are generated at the metal-film interface. But there are plenty of metal-electrolyte or metal-gas systems where film growth does occur mainly by **cation** migration, so such systems should show SCC. Perhaps they do – no-one has done a systematic study. Of course, anodic SCC mechanisms have a much more natural rationalisation – in the passive state, and with rapid repassivation of bare surfaces, the environment is excluded from the metal.

Metal/metal-ion equilibrium systems

An interesting development in the surface mobility model came about through the observation of SCC in alloys, at or close to the equilibrium potential of the more noble alloy component. Actually this was not a new observation at all /Bertocci et al. 1984, Sieradzki et al. 1987/, but the resultant cracking from film-free, “uncontaminated” surfaces prompted an appeal to the *exchange current density* as a factor likely to enhance surface mobility /Galvele 2000/. The following equation was derived:

$$D_s = \frac{i_0 N_A A n^2 a^4}{6F} \quad 3-13$$

where i_0 is the exchange current density, N_A is Avogadro’s number, A is the atom fraction of base (reactive) metal atoms in the alloy (this was called AF in the original paper), n is a kind of dimensionless distance or average hop size, a is the atom size, and the 6 arises because this is the number of neighbouring sites in a close-packed plane.

Eventually SCC, at a very low rate, was observed in pure copper and silver, close to equilibrium in solutions of their own salts /Farina et al. 2005/. For copper, the solution used for SCC testing was Cu(II) nitrate – actually a solution in which copper is **not** at equilibrium – if it tries to reach the Cu/Cu⁺⁺ equilibrium potential, it would be corroding, slowly, to Cu₂O as can be seen from the Pourbaix diagram for Cu-H₂O (Figure 3-9). Galvele never examined acidified solutions of copper salts where a bare metal surface, and a true equilibrium, exists. However the result for silver is reasonable evidence that such cracking from a bare metal surface close to the equilibrium potential is feasible.

As usual, there are alternative explanations for the data. No current measurements were reported, but it is quite likely that a straining metal or crack tip at its nominal equilibrium potential will sustain an anodic current. This was a topic that used to be debated many years ago but has become inactive lately. Galvele himself, in his 1993 reworking of the surface mobility model /Galvele 1993/, argued at length that such a mechanism could not account for SCC, but he was not thinking of a system with a crack velocity as low as 10⁻¹⁰ m/s, as was observed for pure silver in his later work.

Actually if the Galvele group had used acidified copper sulphate solution to examine SCC of copper, they could have used the D_s estimation of /Martins et al. 1996/, namely 7 x 10⁻¹⁷ cm²/s (7 x 10⁻²¹ m²/s). With a generic stress value of say 300 MPa, this could give a crack velocity in the region of 2 x 10⁻¹² m/s according to Equation 3-11.

Copper, with or without sulphide ions

For copper exposed to a very dilute sulphide-containing solution, the situation is somewhat different. The reaction of interest is solid-state sulphidation; there is little or no dissolution – although soluble complexes do exist, and may become significant in relatively concentrated sulphide solutions /Smith 2007/. The melting point of Cu₂S is almost the same as that of copper metal – about 1,100°C – with some variation due to variable stoichiometry, so it is not one of those compounds that would be expected to give rapid SCC according to surface mobility. It should not change the cracking propensity as compared with unreacted, bare copper.

So what about the situation that is usually considered to be perfectly safe for copper, namely a reducing environment without even sulphide to cause an anodic reaction? What would be the prediction of the surface mobility model in that case?

Since the canister will not be actively loaded in a manner that could cause huge stresses at the crack tip (we are following the argument of /Serebrinsky and Galvele 2004/ – in reality there may be no such dependence of crack-tip stress on strain rate), it is safe to assume that the stress could not exceed about 300 MPa, which is about the ultimate tensile strength of mildly cold worked copper. Substituting this into equation 3-11, with $T = 350$ K, $D_s = 3.5 \times 10^{-17}$ m²/s (most conservative vacuum D_s value), $a = 2.7 \times 10^{-10}$ m, $L = 10^{-8}$ m, we obtain a cpr of 8.4×10^{-9} m/s – which is high to say the least (264 mm/year). Using the extrapolated Martins diffusion data /Martins et al. 1996/ for electrolyte (sulphuric acid), we obtain 2.6 mm/year.

Obviously, the surface mobility model could never be used to rule out SCC because it will always predict an unacceptable crack propagation rate, even under reducing conditions and in a ‘non-interacting’ electrolyte. But what we can say is that, were cracking to occur by surface mobility, sulphidation should not affect the velocity.

So far as theory is concerned, if we use Sieradzki’s corrected expression for the change in vacancy formation energy ($s^2 a^3 / 2EkT$), in place of sa^3/kT in equation 3-11, and using the same parameters as we just used to get 264 mm/year, we obtain a cpr of 5.6×10^{-12} m/s or 175 mm/year. Because both the exponentials are nearly linear (e^x with small x), the ratio of these velocities is approximately $2E/s$. Using the Martins electrolyte-diffusion data, we obtain 1.75 mm/year. However, it is not sufficient to substitute Sieradzki’s modified vacancy formation energy – this was only one of his problems with the model. He also argued as well that cracks sharper than about 1–10 nm would close up owing to capillary effects. If we use Sieradzki’s modified crack-growth equation:

$$V_n \cong \frac{D_s N_s \Omega^2}{kT} \frac{2}{\pi} \frac{1}{\rho^2} \left(\frac{\sigma_{yy}^2}{2E} - \gamma\kappa \right) \quad 3-14$$

and substitute, where appropriate, reasonable or slightly pessimistic values for all the parameters:

$$D_s = 10^{-17} \text{ m}^2 \text{ s}^{-1}$$

$$N_s = 10^{19} \text{ m}^{-2}$$

$$\Omega = 3 \times 10^{-29} \text{ m}^3$$

$$k = 1.38 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$$

$$T = 350 \text{ K}$$

$$\sigma_{yy} = 300 \text{ MPa}$$

$$E = 120 \text{ GPa}$$

$$\gamma = 1.5 \text{ J m}^{-2}$$

and maximise $\frac{1}{\rho^2} \left(\frac{\sigma_{yy}^2}{2E} - \gamma\kappa \right)$ by placing its differential equal to 0 (which gives $r = 6.5$ mm, which would be considered very blunt), then we obtain V_n about 4×10^{-20} m s⁻¹!

Clearly, the surface mobility model, correctly formulated as claimed by Sieradzki, cannot result in failure of the canister by SCC over a period of one million years.

Appendix B describes the application of the surface mobility model to the SCC of copper in gaseous systems. It is concluded that whilst these are interesting cracking phenomena, they are much more likely to be due to fast ion transport in oxides at grain boundaries (similar to “tarnish rupture”) than to the usual form of the surface mobility mechanism

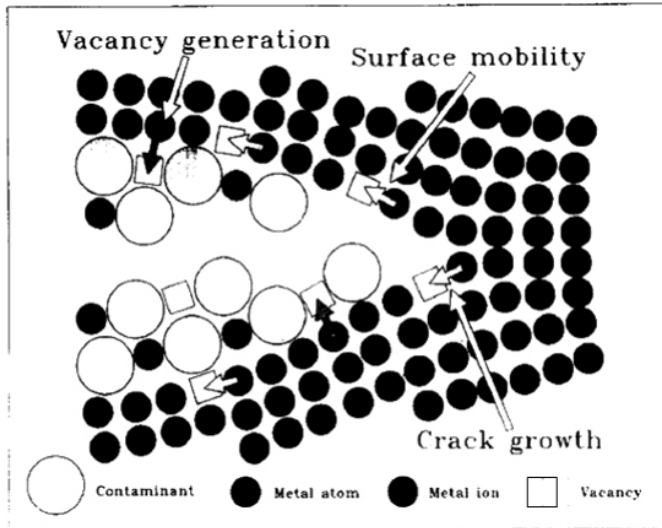


Figure 3-8. Crack propagation by surface mobility, according to Galvele.

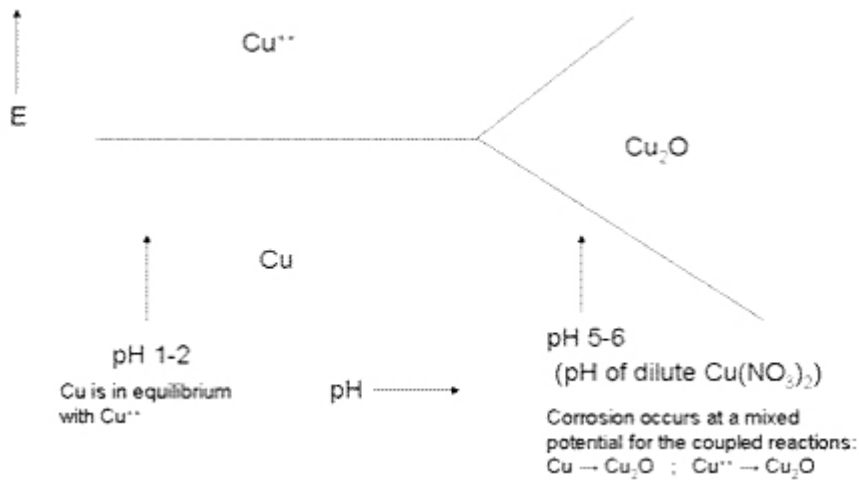


Figure 3-9. Detail of the Pourbaix diagram for copper, showing that in an unacidified system containing Cu²⁺, copper does not adopt an equilibrium potential; thus the observation of SCC of pure Cu in unacidified, aqueous Cu(NO₃)₂ solution /Farina et al. 2005/ is not an ‘equilibrium’ experiment.

3.5 Other mechanisms

Adsorption-induced dislocation emission, crack-tip vacancy formation, and other non-standard proposals

According to Lynch (private communication), ‘surface mobility’ can be harmonised with a mechanism of crack growth /Lynch 2007/ wherein adsorption of species from the environment, including hydrogen, facilitates dislocation emission from the crack tip. As he points out, both mechanisms involve the weakening of bonds between metal atoms, and some proportionality between the resulting crack growth rates might be expected. A strength of Lynch’s proposal is that it easily encompasses liquid metal and hydrogen embrittlement, whereas these are treated a little vaguely in the surface mobility model. Like Galvele, Lynch cites particular experiments showing very high crack velocities, but with more justification, in that the cracking of nickel monocrystals in mercury or hydrogen does seem to be a continuous process, without the crack jumps that can be demonstrated in at least some of the conditions (e.g. AuAg, PdAg, AgCd), where Galvele claims a rapid, continuous crack growth.

From an energetic point of view, the Lynch mechanism, or AIDE (Adsorption Induced Dislocation Emission) /Lynch 2007/ relies on the occurrence of intense plasticity within a very small volume at the crack tip. This can lower the total energy of fracture, which is integrated over the whole deformed volume around the crack.

A weakness of the AIDE mechanism used to be the insistence on a truly 2D interaction rather than any 3D reaction mechanism. Nowadays, Lynch tends to accommodate a near-surface process zone, although in the case of liquid metal embrittlement in immiscible systems, this must be very shallow. An intriguing suggestion, based on first-principles calculations for Ga on Al, is that liquid metal embrittlement (LME) systems are those in which there is alloying of the liquid metal into the first one or two atomic layers of the substrate /Stumpf and Feibelman 1996/. Since surface alloying is also known in vacuum deposition and in underpotential deposition of metals on copper and other metals /Robert et al. 1996, Tersoff 1995/, this raises the interesting possibility that traces of Pb ions could cause cracking of copper by an underpotential displacement reaction followed by a LME-type cracking. Unlike other kinds of cracking, this would be positively assisted by the establishment of reducing conditions. Fortunately Pb^{++} and similar ions do not appear to be present in the repository at levels that could credibly cause such a cracking mechanism (e.g. ppm at least).

One of several ‘orphan’ SCC models is that of Aaltonen and others in Finland, based on internal friction studies /Aaltonen et al. 1998, Jagodzinski et al. 2000/. These results are so surprising (much more so, we would submit, than film-induced cleavage) that no other author has seriously addressed them. Essentially, these authors showed that anodic polarisation of copper wires at room temperature in a sodium nitrite solution, under conditions promoting duplex Cu(I)-Cu(II) oxide formation, produced defects that behaved like vacancies under the standard protocols used for internal friction measurement. Later, /Aaltonen et al. 2003/ reported an increase in creep rate under similar conditions. One’s immediate reaction is that even if such vacancies were to be produced, they must be confined within nanometres of the metal-film interface, so how is it possible for this nm-thick layer to dominate the internal friction response when the smallest sample dimension is 0.5 mm? Yet the results are quite striking, showing Hasiguti peaks in the anodically treated samples. One possibility (acting as devil’s advocate) is that there is an autoreduction or disproportionation of a thick oxide, that produces metallic copper with a high defect density. Yet even in that case, the defected metallic layer would be a tiny fraction of the total sample dimension. But we should certainly not dismiss such observations. Most people do not know that oxygen has vast mobility in silver at room temperature, and something like that, rather than conventional vacancy diffusion, might be the answer. Still, until the Aaltonen work receives a proper international discussion, it is likely to remain an interesting curiosity. Of course this is partly the authors’ own fault – they could have examined oxides formed by a variety of methods, reduced them, and so on. Their correlation between vacancy injection and SCC is weak because it is so specialised.

In any event, the Aaltonen mechanism is one that should not operate at reducing potentials, unless perhaps associated with a sulphide film.

Other authors have cited the formation of vacancies at crack tips without claiming direct evidence of their formation, which is the unique aspect of the Aaltonen study. /Meletis and Lian 1995/ did interesting work on copper SCC but there was no compelling cause-and-effect. The late Denny Jones used to

cite vacancy formation during anodic dissolution, and carried out ingenious experiments with thin-film bimetallic multilayers that were dissolved and then subjected to Auger depth profiling, claiming that interdiffusion zones were present – the status of this work is unclear in view of the complexities of such depth profiling /Jones et al. 1997/. In Appendix A, we note however that in its recently understood formulation, the surface mobility model is really a vacancy injection model (since the site of vacancy accumulation is assumed to be ahead of the crack tip, not at the crack tip surface), so some coming together would be welcome.

3.6 Summary of mechanistic observations

The mechanisms considered above included:

1. Film rupture /Jones 1992/
2. Tarnish rupture /Escalante and Kruger 1971, Suzuki and Hisamatsu 1981/
3. Surface mobility /Galvele 1987, 1993, 1996, 2000/
4. Film-induced cleavage or intergranular fracture /Newman and Sieradzki 1987, Sieradzki and Newman 1985, 1987/
5. Adsorption-induced dislocation emission /Lynch 2007/
6. Vacancy injection and embrittlement /Aaltonen et al. 1998, 2003, Jagodzinski et al. 2000/

along with aspects of dissolution and sulphide film formation.

The conclusions are:

- The classic film rupture and tarnish rupture mechanisms require the presence of a Cu_2O film and sufficient crack-tip strain to either rupture the film to allow crack growth by dissolution or to fracture the tarnish to promote crack growth /Jones 1992/.
- These classic mechanisms would only appear to be possible for a limited period during the evolution of the repository environment. The eventual onset of anaerobic and saline conditions in the pore water will lead to the dissolution of a previously formed oxide /King et al. 2010/.
- Sulphide ions are unlikely to support either film rupture or tarnish rupture mechanisms in the repository, not least because there will be no sulphide in the crack as the supply of sulphide to the free surface will be diffusion limited through the compacted bentonite /King et al. 2010, SKB 2006/.
- The surface mobility model, as currently formulated, would predict a certain crack velocity for copper with no chemical environment at all. Cu(I) sulphide has a melting point similar to that of copper, so it would not be expected to influence the crack velocity on that basis.
- The surface mobility model appears to have been incorrectly formulated on at least two levels /Sieradzki and Friedersdorf 1994/. First, the expression used for the reduction in vacancy formation energy by stress is appropriate for the bulk solid, not a free surface. This, if corrected as attempted by /Sieradzki and Friedersdorf 1994/, reduces the predicted crack velocities by about 2 orders of magnitude. But Galvele claimed since 1993 that the vacancy sink was inside the solid, albeit only a few atom spacings from the crack tip (justifying, on tenuous grounds, the use of the bulk-lattice energetics), and that anyway a model based on the free surface vacancies should not be based on equilibrium vacancy concentrations. However, consideration of the true radii of crack tips will likely invalidate any such approach. Second, the model ignores a capillary term which in this type of creep cracking would cause sharp cracks to close up. According to Sieradzki's analysis, the crack velocity in copper at 350 K should be vanishingly small.
- Observations of intergranular SCC in copper exposed to cupric nitrate solution, by the Galvele group /Farina et al. 2005/, were not made under film-free conditions – a Cu_2O film is formed, and allies this (very slow) cracking more closely with film-rupture systems. Also such cracking is likely absent under static loading.
- Film-induced cleavage is probably always operative with some kind of nanoporous metal layer or hybrid oxide-porous metal interface. It is not out of the question to suggest that such porosity could form in a sulphide system, but there is no evidence one way or the other. The sulphide film itself is not likely a suitable initiating layer.

- The vacancy injection model of /Aaltonen et al. 1998, 2003/ is based on intriguing internal friction measurements made on copper in nitrite solution. This deserves further attention, but the nitrite system is in any case a peculiar one and it is improbable that anything similar could happen in dilute sulphide.
- The Lynch model is a 'universal' one, and according to /Lynch 2007/ might be related in a general conceptual way to surface mobility, in that dislocation emission is more likely from a mobile surface (but sulphide should make the surface relatively immobile). Again, such concepts are very seriously based and deserve further attention.
- The reported intergranular SCC of copper in sulphide solution /Taniguchi and Kawasaki 2008/ likely does not occur by any of these mechanisms, but by intergranular sulphidation (film-rupture type SCC) under extreme mechanical conditions.
- All known true SCC phenomena mechanisms in copper are very dependent on dynamic tensile strain, especially the transgranular variants. This is likely also true of the recently discovered 'sulphide-induced SCC' of /Taniguchi and Kawasaki 2008/.

4 Studies of the SCC of copper under repository conditions

/King et al. 2001, 2010/ summarised a number of studies performed specifically to investigate the SCC behaviour of copper canisters. These authors concluded that the probability of SCC of a Cu canister will diminish with time as the repository environment evolves. Early in the evolution of the repository, conditions may be at their most suitable for SCC as it is during this period that oxidant will be available (in the form of O_2 and/or $Cu(II)$), Cu_2O films will be stable on the canister surface, and the copper shell could be subject to strain as it deforms onto the inner cast iron insert under the external swelling pressure and hydrostatic loads. Furthermore, although not discussed in detail here, Cl^- ions appear to have an inhibitive effect on the SCC of copper alloys, and the pore-water salinity will be most dilute initially, prior to saturation of the bentonite by saline groundwater. Once the copper shell has deformed onto the inner vessel and as the environmental conditions become more benign, the probability of SCC is likely to diminish.

A number of other studies have appeared since the 2001 report and are summarised here.

Work in the Canadian nuclear waste disposal program has focused on experimental studies of the SCC of OFP Cu in the three environments known to support cracking /Ikeda and Litke 2004, 2007, 2008, Litke and Ikeda 2006, 2008/ and the development of a predictive model /King and Kolar 2004, 2005, Maak and King 2005/. The major conclusions from the experimental work are:

1. except under the most aggressive conditions, OFP copper exhibits largely ductile behaviour in ammonia, acetate, and nitrite solutions /Ikeda and Litke 2004, 2007, 2008, Litke and Ikeda 2006, 2008/,
2. only specimens covered by a visible surface oxide exhibited cracking and only at potentials and pH values consistent with a Cu_2O film /Ikeda and Litke 2004/,
3. the presence of Cl^- ions inhibits the SCC of OFP copper /Ikeda and Litke 2004, 2007, 2008, Litke and Ikeda 2006/, and
4. in nitrite solutions, the susceptibility to cracking decreases with increasing temperature /Ikeda and Litke 2007/.

The observation that cracking is only observed at certain values of the potential and pH has been used as the basis for a predictive model for the SCC of copper canisters /King and Kolar 2004, 2005, Maak and King 2005/. Phenomenologically, cracking is only observed if the combination of the pH of the **bulk solution** and the potential of the **free surface** lie above the equilibrium line for the Cu_2O/CuO couple (Figures 4-1 to 4-3). It is neither suggested in the model that a duplex Cu_2O/CuO film is in any way associated with cracking nor implied that the pH and potential outside of the crack indicate conditions at the crack tip. Instead, the observations are used as a convenient method for predicting the period during the evolution of the repository environment when the conditions at the external surface of the canister could be suitable to support cracking. (Note: the apparent instances of cracking in acetate solutions at pH 5.5 that lie below the Cu_2O/CuO equilibrium line (Figure 4-2) are considered to represent experimental scatter).

With this as a basis for the model, the prediction involves the estimation of the time dependence of the corrosion potential (E_{CORR}) of the canister and of the interfacial pH. A modified version of the Copper Corrosion Model /King and Kolar 2000, King et al. 2008/ is used to predict E_{CORR} and the interfacial pH, the latter based on the gain and loss of OH^- ions due to the various interfacial electrochemical and precipitation/dissolution reactions at the canister surface.

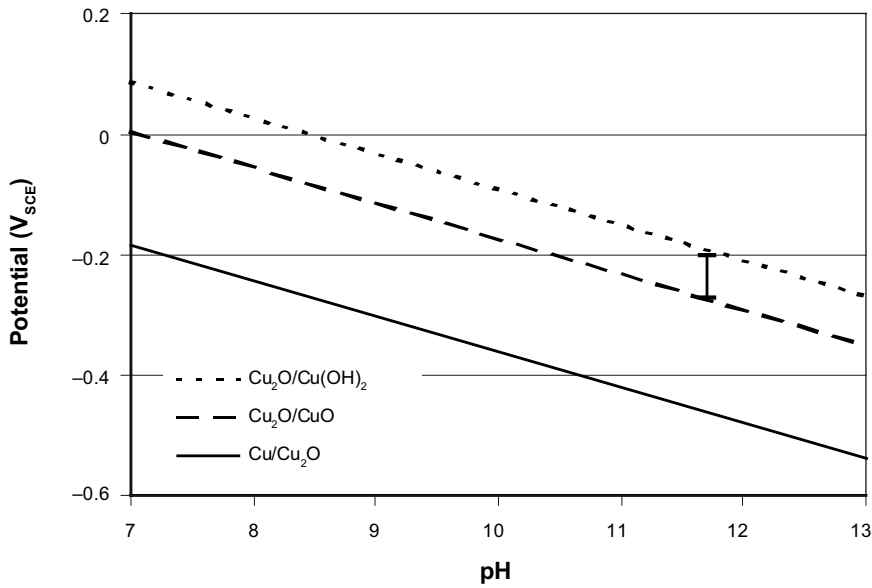


Figure 4-1. Comparison of the potential and pH dependence for the SCC of copper in 1 mol/L ammonia solution with the equilibrium potentials for Cu/Cu₂O, Cu₂O/CuO, and Cu₂O/Cu(OH)₂ /King and Kolar 2004, 2005/. The range of potentials for SCC is taken from /Ikeda and Litke 2004/.

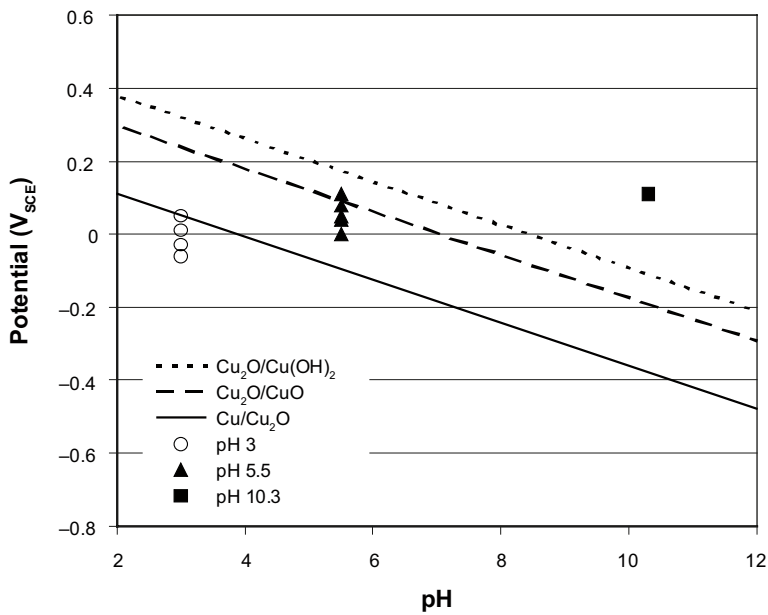


Figure 4-2. Comparison of the pH and potential dependence for SCC in 0.1 mol/L sodium acetate solution and the equilibrium potentials for Cu/Cu₂O, Cu₂O/CuO, and Cu₂O/Cu(OH)₂ /King and Kolar 2004, 2005/ (SCC data from /Cassagne et al. 1990/). Cracking observed at pH 5.5 and 10.3 (full symbols), no SCC observed at pH 3 (open symbols).

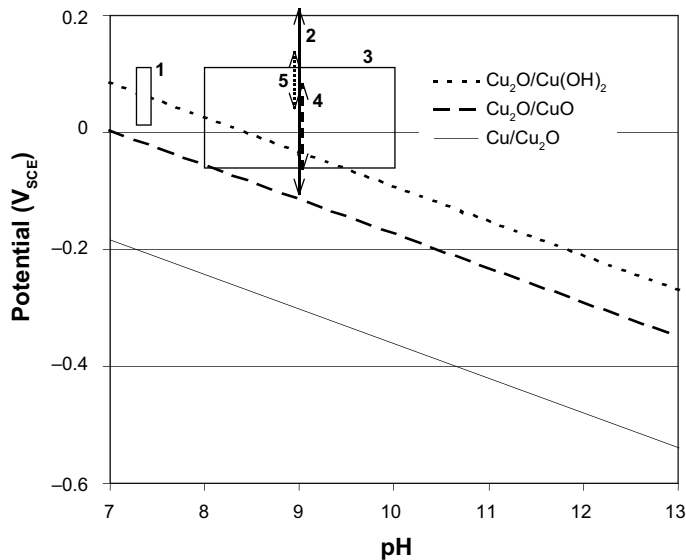


Figure 4-3. Comparison of the potential and pH dependence for the SCC of copper in nitrite solutions with the equilibrium potentials for $\text{Cu}/\text{Cu}_2\text{O}$, $\text{Cu}_2\text{O}/\text{CuO}$, and $\text{Cu}_2\text{O}/\text{Cu}(\text{OH})_2$ /King and Kolar 2004, 2005/. The various ranges for SCC are taken from; 1: /Uchida et al. 1991/, 2: /Yu and Parkins 1987/, 3: /Benjamin et al. 1988/, 4: /Cassagne et al. 1990/, and 5: /Ikeda and Litke 2000/.

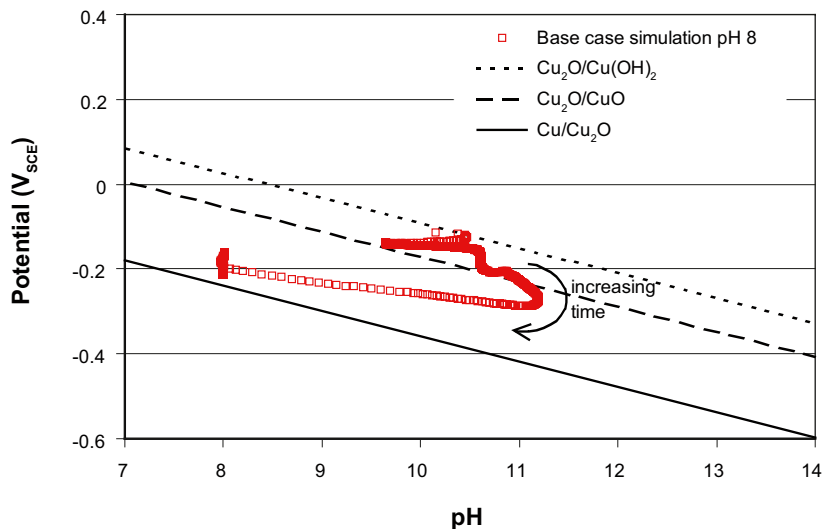


Figure 4-4. Predicted time dependence of the corrosion potential and interfacial pH for a copper canister in a Canadian-design deep geologic repository based on the Copper Corrosion Model for Stress Corrosion Cracking (CCM-SCC) /King and Kolar 2005/.

Figure 4-4 shows the results of such a prediction for a copper canister in a Canadian deep geologic repository of a similar design to that proposed in Sweden. The interfacial pH is initially high (>pH 10) due to O_2 reduction on the canister surface and the homogeneous oxidation of $\text{Cu}(\text{I})$ to $\text{Cu}(\text{II})$ at the canister/bentonite interface. However, the interfacial pH drops quickly as the flux of O_2 to the canister surface diminishes. The period of time for which the combination of E_{CORR} and pH is greater than the $\text{Cu}_2\text{O}/\text{CuO}$ equilibrium line in Figure 4-4 is less than three years following canister deposition.

A secondary line of argument in the model is that the interfacial concentrations of SCC agents, namely ammonia, acetate, and nitrite ions, are insignificant. Microbial activity is considered to be the only source for these species since none is present naturally in Swedish groundwaters. Given the restrictions on microbial activity in highly compacted bentonite /King and Kolar 2006/, the maximum interfacial concentration of any of these SCC agents is predicted to be $<10^{-10}$ mol/L, from which it is concluded that SCC would not occur, regardless of the extent of tensile strain on the canister surface. Recent measurements /Masurat et al. 2010/ suggest that some microbially mediated sulphate reduction is possible in compacted bentonite before the development of the full swelling pressure, although apparently in amounts insufficient to cause SCC due to sulphide /Taniguchi and Kawasaki 2008/ and with no reports of other SCC agents being produced.

A decision tree was developed based on this approach (Figure 4-5) /King and Kolar 2004, 2005, Maak and King 2005/. The decision tree accounts not only for the need to meet certain E_{CORR} and pH threshold values, but also takes into account the need for SCC agents, the inhibitive effect of Cl^- , the effect of temperature, and the need for tensile strain. A “no” answer to any one of the questions is sufficient to preclude the possibility of SCC.

Work in Finland and Sweden has focused on studies of specific cracking systems. /Kinnunen 2006/ simulated the long-term anaerobic conditions in the repository and considered the possibility of SCC in acetate solutions. Not surprisingly because of the absence of O_2 or $Cu(II)$, he failed to observe any cracking during SSRT in saline groundwaters with the addition of 1-100 mg/L acetate. These tests do suggest, however, that cracking is unlikely under anaerobic conditions, even during severe mechanical deformation. /Khanzhin and Nikulin 2005/ examined the SCC of copper in 0.1 mol/L $NaNO_2$ using a combination of acoustic emission, fractography, and fracture mechanics. The authors were able to separate initiation and propagation stages and to estimate stress intensity factors and J-integrals for the onset of each stage of cracking.

As discussed above, /Taniguchi and Kawasaki 2008/ have recently reported the SCC of pure copper (with 45 ppm P) in synthetic seawater solutions containing sulphide. Experiments were carried out at a temperature of 80°C with 0, 0.001, 0.005, and 0.01 mol/L HS^- , added to solution as Na_2S . Tensile specimens were strained to failure by SSRT at a strain rate of $8 \times 10^{-7} s^{-1}$. The specimens were potentiostatted during the tests at a potential equivalent to the open-circuit potential at the start of the exposure. Loss of ductility was reported at a HS^- concentration of 0.01 mol/L due to intergranular SCC. Only single experiments were reported. From these data, the authors concluded that pure copper is susceptible to SCC in sulphide solutions above a threshold concentration of between 0.005 mol/L and 0.01 mol/L. This concentration is 2-3 orders of magnitude higher than that expected in a Swedish repository (Table 2-1), suggesting that SCC is unlikely under repository conditions especially given that the interfacial sulphide concentration will be close to zero due to mass-transport limitations.

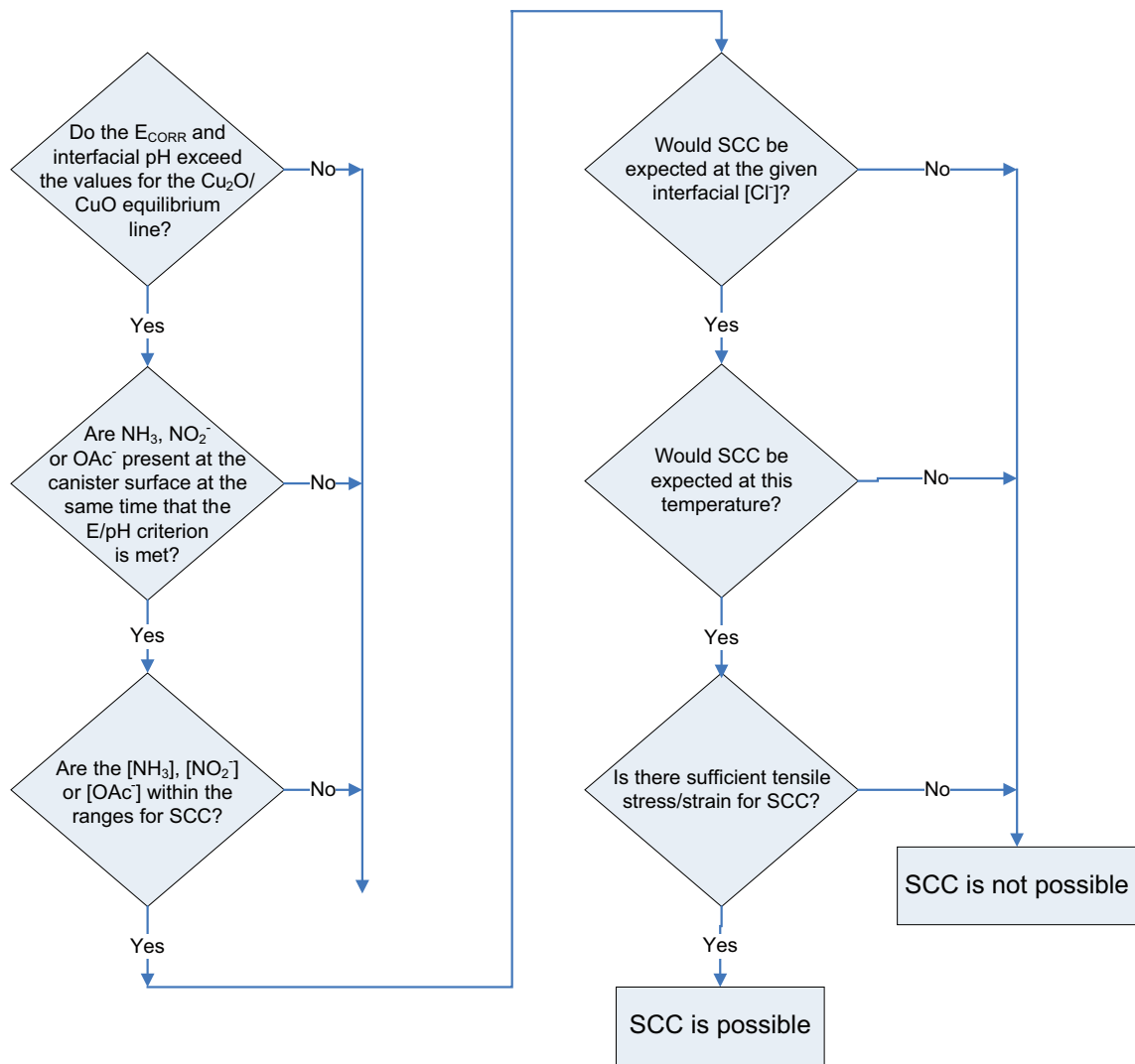


Figure 4-5. Decision tree for determining the susceptibility of copper canisters to stress corrosion cracking /King and Kolar 2004, 2005/.

5 SCC behaviour of copper canisters in a deep geologic repository

There are a number of sources of information on which the long-term SCC behaviour of copper canisters can be predicted:

1. Practical engineering experience with the use of copper alloys in corrosive environments.
2. A combination of mechanistic descriptions of the cracking process coupled with an understanding of the environmental conditions to which the canister will be exposed.
3. Laboratory observations in model systems and inferences from analogous alloy/environment combinations.

Practical engineering experience is a useful indicator of (relatively) short-term susceptibility to SCC, but is generally difficult to extrapolate to the timescales of interest here. The general experience would suggest that copper is only susceptible to cracking in aerobic systems containing significant amounts of ammonia, nitrite, or acetate ions.

A combination of mechanistic understanding and knowledge of how the environment evolves with time is much more amenable to long-term prediction. This approach is typified by the decision tree outlined in Figure 4-5. However, in the manner that it has been applied up until now, this approach cannot address questions such as “Is copper susceptible to SCC in systems other than ammonia, nitrite, and acetate?” It is to answer questions such as this that studies on model systems and analogies to other known cracking systems are useful.

Two periods are considered here; first, the initial aerobic period including the transition phase during which Cu(II) is reduced to Cu(I) and dissolution of the pre-formed Cu₂O occurs and second, the indefinite anaerobic period during which sulphide ions may be present in the near field.

The initial aerobic and transition periods are short enough that practical engineering experience, supported by a mechanistic understanding, is useful in predicting the SCC behaviour of the canister. It is during this period that a number of, but not all, environmental conditions are favourable for cracking. Oxidant is available as either O₂ or Cu(II), the surface will be covered by a Cu₂O film, the Cl⁻ concentration will be low, and the outer Cu shell may undergo dynamic strain as it deforms onto the inner cast iron insert due to the imposition of the hydrostatic and bentonite swelling pressures (during the latter stages of this period). However, the limiting factor will be the absence of any SCC-supporting species, such as ammonia, acetate, or nitrite ions. If all appropriate environmental and mechanical requirements are met, cracking is possible during this period via film rupture, tarnish rupture, or film-induced cleavage mechanisms. As argued above, the formulation of the surface mobility model is believed to be flawed and, in its correct form, would predict crack growth rates too small to be of significance, even on repository timescales.

It could be argued that the absence of SCC agents is not a sufficient argument to discount the possibility of cracking since other, as yet unknown, species may also support cracking. However, since the period of practical engineering experience with the SCC of copper alloys (approximately 100–150 years) is equal to or greater than the duration of the initial aerobic period, it is reasonable to claim that all species known to cause rapid cracking of copper alloys have been identified.

It is during the indefinite anaerobic phase that we cannot rely on practical engineering experience to extrapolate the SCC behaviour over the very long term. In order to justify predictions over tens and hundreds of thousands of years, we must rely not only on a mechanistic understanding but also our basic understanding of cracking phenomena in other alloy systems. The questions to be answered are:

1. would the known mechanisms for the SCC of copper support cracking under anaerobic conditions, particularly in the presence of sulphide, and
2. by analogy with other alloys systems, is there any other process or mechanism that could result in SCC in the long term?

Both the film rupture and tarnish rupture mechanisms require dissolution and film formation in the crack itself to sustain cracking. Under anaerobic conditions, the only oxidant present is H₂O in the presence of HS⁻ ions. Cuprous oxide is not stable under these conditions and, as noted above, sulphide will not be present in the crack since it is under diffusion-limited control to the free surface in compacted bentonite. Therefore, SCC via either of these two mechanisms is not possible.

Sulphide films, typically being non-adherent /Smith 2007/, would appear to be unsuitable for sustaining cracking by a film-induced cleavage mechanism. Furthermore, the development of the type of nanoporous surface layer that does support film-induced cleavage requires relatively rapid rates of dissolution, because otherwise the porous layer coarsens through surface diffusion. Once again, because the rate of corrosion under anaerobic conditions will be transport-limited by diffusion of HS⁻ through the bentonite, it is unlikely that the necessary nanoporous layers will be formed.

As noted above, the formulation of the surface mobility model is considered to be flawed, such that even if cracking does occur by this mechanism the rates will be vanishingly small, even on repository timescales ($\sim 10^{-20}$ m/s). Furthermore, based on a comparison of melting points, the presence of HS⁻ will not lead to more rapid surface diffusion and hence more rapid cracking.

We have also discussed two mechanisms that are still under development, the adsorption-induced dislocation emission and vacancy injection and embrittlement models. Whilst both models are plausible from a scientific viewpoint, there is no evidence that the presence of HS⁻ would make cracking more likely.

Therefore, we are left to conclude that there is no well-founded SCC mechanism that would result in cracking during the long-term anaerobic phase in the repository.

6 Conclusions

The possibility of stress corrosion cracking (SCC) of copper canisters in a deep geological repository in the Fennoscandian Shield has been assessed. Each of the four main mechanisms proposed for the SCC of pure copper, film rupture (slip dissolution), tarnish rupture, film-induced cleavage, and surface mobility, have been reviewed. The required conditions for cracking for each mechanism have been compared with the expected environmental and mechanical loading conditions within the repository. Other SCC mechanisms currently under development have also been considered.

Mechanisms that require a degree of oxidation or dissolution are only possible whilst oxidant is present in the repository and then only if other environmental and mechanical loading conditions are satisfied. These constraints are found to limit the period during which the canisters could be susceptible to cracking via film rupture or tarnish rupture mechanisms to the first few years after deposition of the canisters. However, there will be insufficient SCC agent (ammonia, acetate, or nitrite) to support cracking during this period. During the anaerobic phase, the supply of sulphide ions to the free surface will be transport limited by diffusion through the highly compacted bentonite. Therefore, no HS^- will enter the crack and cracking by either of these mechanisms in the long term is not feasible.

Cracking via the film-induced cleavage mechanism requires a surface film of specific properties, typically a nanoporous structure. Slow rates of dissolution characteristic of processes in the repository will tend to coarsen any nanoporous layer. Under some circumstances, a cuprous oxide film could support film-induced cleavage, but there is no evidence that this mechanism would operate during the long-term anaerobic period because copper sulphide films appear to be insufficiently adherent.

A critical review of the surface mobility model has been presented. The formulation of the crack growth law appears to be flawed and in its corrected form predicts crack growth rates of the order of 10^{-20} m/s. Therefore, even if cracking were to occur via this mechanism, the crack velocity would be too small to lead to canister failure, even over repository timescales.

Two other SCC mechanisms, the adsorption-induced dislocation emission and vacancy injection and embrittlement models, have also been discussed. Although these models are still in the development stage, it is considered unlikely that they could induce cracking during the long-term anaerobic phase.

Therefore, it is concluded that the probability of SCC during the early aerobic period is low because of the absence of the necessary conditions for cracking and that there is no well-founded SCC mechanism that would result in cracking during the long-term anaerobic phase in the repository.

References

SKB's (Svensk Kärnbränslehantering AB) publications can be found at www.skb.se/publications.

- Aaltonen P, Jagodzinski Y, Tarasenko A, Smouk S, Hänninen H, 1998.** Low-frequency internal friction of pure copper after anodic polarisation in sodium nitrite solution. *Corrosion Science*, 40, pp 903–908.
- Aaltonen P, Jagodzinski Y, Hanninen H, 2003.** Vacancy generation in electrochemical oxidation/dissolution of copper in NaNO_2 solution and its role in SCC mechanism. In: Proceedings of the International Conference on Hydrogen Effects on Materials Behavior and Corrosion Deformation Interactions, Moran, Wyoming, 22–26 September, 2002 Warrendale, PA: TMS-AIME, pp 597–606.
- Andresen P L, Ford F P, 1988.** Life prediction by mechanistic modeling and system monitoring of environmental cracking of iron and nickel alloys in aqueous systems. *Materials Science and Engineering*, A103, pp 167–184.
- Baier S, Dieluweit S, Giesen M, 2002.** Step and island dynamics on Cu(111), Ag(111) and Au(100) electrodes in electrolyte. *Surface Science*, 502–503, pp 463–473.
- Barnes A, Senior N A, Newman R C, 2008.** Revisiting the film-induced cleavage model of SCC. In: Shipilov S A, Jones R H, Olive J-M, Rebak R B (eds). *Environment-induced cracking of materials: proceedings of the Second International Conference on Environment-Induced Cracking of Metals (EICM-2)*, Banff, Alberta, Canada, 19–23 September 2004. Vol. 1. Amsterdam: Elsevier, pp 47–58.
- Barthes M G, Rhead G E, 1978.** *Comptes Rendus Hebdomadaires des Séances de l'Académie des sciences, Série C*, 287, pp 539–541.
- Beavers J A, Pugh E N, 1980.** The propagation of transgranular stress-corrosion cracks in admiralty metal. *Metallurgical and Materials Transactions A*, 11, pp 809–820.
- Benjamin L A, Hardie D, Parkins R N, 1988.** Stress corrosion resistance of pure coppers in ground waters and sodium nitrite solutions. *British Corrosion Journal*, 23, pp 89–95.
- Bertocci U, Thomas F I, Pugh E N, 1984.** Stress corrosion cracking of brass in aqueous ammonia in the absence of detectable anodic dissolution. *Corrosion*, 40, pp 439–440.
- Cassagne T B, Kruger J, Pugh E N, 1990.** Role of the oxide film in the transgranular stress corrosion cracking of copper. In: Lisagor W B, Crooker T W, Leis B N (eds). *Environmentally assisted cracking: science and engineering*. Philadelphia: American Society for Testing and Materials. (ASTM special technical publication 1049), pp 59–75.
- Davanas K, Solomon A A, 1990.** Theory of intergranular creep cavity nucleation, growth and interaction. *Acta Metallurgica et Materialia*, 38, pp 1905–1916.
- Delamare F, Rhead G E, 1971.** Increase in the surface self-diffusion of copper due to the chemisorption of halogens. *Surface Science*, 28, pp 267–284.
- Doña J M, González-Velasco J, 1992.** The dependence of the surface diffusion coefficients of gold atoms on the potential: its influence on reconstruction of metal lattices. *Surface Science*, 274, pp 205–214. (Erratum published in *Surface Science* 282, p 202.)
- Dursun A, Pugh D V, Corcoran S G, 2003.** Dealloying of Ag-Au alloys in halide-containing electrolytes: affect on critical potential and pore size. *Journal of the Electrochemical Society*, 150, pp B355–B360.
- Edeleanu C, Forty A J, 1960.** Some observations on the stress-corrosion cracking of a-brass and similar alloys. *Philosophical Magazine*, 58, pp 1029–1040.
- EPRI, 2007.** Proceedings of a Workshop on Effects of Cold Work on SCC of Nuclear Materials, Mississauga, Ontario, 3–8 June 2007. Palo Alto, CA: EPRI.
- Escalante E, Kruger J, 1971.** Stress corrosion cracking of pure copper. *Journal of the Electrochemical Society*, 118, pp 1062–1066.

- Farina S B, Duffó G S, Galvele J R, 2005.** Stress corrosion cracking of copper and silver, specific effects of the metal cations. *Corrosion Science*, 47, pp 239–245.
- Flanagan W F, Zhong L, Lichter B D, 1993.** A mechanism for transgranular stress-corrosion cracking. *Metallurgical and Materials Transactions A*, 24, pp 553–559.
- Galvele J R, 1987.** A stress corrosion cracking mechanism based on surface mobility. *Corrosion Science*, 27, pp 1–33.
- Galvele J R, 1993.** Surface mobility mechanism of stress-corrosion cracking. *Corrosion Science*, 35, pp 419–434.
- Galvele J R, 1996.** Application of the surface-mobility stress corrosion cracking mechanism to nuclear materials. *Journal of Nuclear Materials*, 229, pp 139–148.
- Galvele J R, 2000.** Recent developments in the surface-mobility stress-corrosion-cracking mechanism. *Electrochimica Acta*, 45, pp 3537–3541.
- Giesen M, 2001.** Step and island dynamics at solid/vacuum and solid/liquid interfaces. *Progress in Surface Science*, 68, pp 1–154.
- Gontier-Moya E G, Beszeda I, Moya F, 2004.** Comparisons of parameters involved in mass transport and desorption at the surface of noble metals and sapphire. *Surface Science*, 566–568, pp 148–154.
- Heldt J, Seifert H P, 2000.** Stress corrosion cracking of reactor pressure vessel steels under boiling water reactor conditions. In: Bruemmer S, Ford P, Was G (eds). *Proceedings of the ninth International Symposium on Environmental Degradation of Materials in Nuclear Power Systems – Water Reactors*, Newport Beach, CA, 1–5 August 1999. Warrendale, PA: Minerals, Metals & Materials Society, pp 901–910.
- Herring C, 1950.** Diffusional viscosity of a polycrystalline solid. *Journal of Applied Physics*, 21, pp 437–445.
- Ikeda B M, Litke C D, 2000.** The effect of oxidant flux, nitrite concentration and chloride concentration on the stress corrosion cracking behaviour of non-welded and electron-beam welded copper. Report 06819-REP-01200-10049-R00, Ontario Power Generation, Nuclear Waste Management Division, Canada.
- Ikeda B M, Litke C D, 2004.** Status report for 2003 on stress corrosion cracking of OFP copper in ammonia. Report 06819-REP-01300-10078, Ontario Power Generation, Canada.
- Ikeda B M, Litke C D, 2007.** Stress corrosion cracking of copper in nitrite/chloride mixtures at elevated temperatures. NWMO TR-2007-04, Nuclear Waste Management Organization, Canada.
- Ikeda B M, Litke C D, 2008.** The effect of high chloride concentration on stress corrosion cracking behavior of copper. NWMO TR-2008-12, Nuclear Waste Management Organization, Canada.
- Jagodzinski Y, Aaltonen P, Smouk S, Tarasenko A, Hänninen H, 2000.** Internal friction study of environmental effects on metals and alloys. *Journal of Alloys and Compounds*, 310, pp 256–260.
- Jones D A, Jankowski A F, Davidson G A, 1997.** Room-temperature diffusion in Cu/Ag thin-film couples caused by anodic dissolution. *Metallurgical and Materials Transactions A*, 28, pp 843–850.
- Jones R H (ed), 1992.** Stress-corrosion cracking. Materials Park, OH: ASM International.
- Kelly R G, Frost A J, Shahrabi T, Newman R C, 1991.** Brittle fracture of an Au/Ag alloy induced by a surface film. *Metallurgical and Materials Transactions A*, 22, pp 531–541.
- Kelly R G, Young A J, Newman R C, 1993.** The characterization of the coarsening of dealloyed layers by EIS and its correlation with stress-corrosion cracking. In: Scully J R, Silverman D C, Kendig M W (eds). *Electrochemical impedance: analysis and interpretation*. Philadelphia, PA: American Society for Testing and Materials. (ASTM special technical publication 1188), pp 94–112.
- Khazhin V G, Nikulin S A, 2005.** Assessment of copper resistance to stress-corrosion cracking in nitrite solutions by means of joint analysis of acoustic emission measurements, deformation diagrams, qualitative and quantitative fractography, and non-linear fracture mechanics. SKB TR-05-15, Svensk Kärnbränslehantering AB.

- King F, 1996.** The potential for stress corrosion cracking of copper containers in a Canadian nuclear fuel waste disposal vault. Report AECL-11550, COG-96-94, Atomic Energy of Canada Limited.
- King F, Kolar M, 2000.** The copper container corrosion model used in AECL's second case study. Report 06819-REP-01200-10041-R00, Ontario Power Generation, Nuclear Waste Management Division, Canada.
- King F, Kolar M, 2004.** Theory manual for the copper corrosion model for stress corrosion cracking of used fuel disposal containers CCM-SCC.0. Report 06819-REP-01300-10095, Ontario Power Generation, Nuclear Waste Management Division, Canada.
- King F, Kolar M, 2005.** Preliminary assessment of the stress corrosion cracking of used fuel disposal containers using the CCM-SCC.0 model. Report 06819-REP-01300-10103, Ontario Power Generation, Nuclear Waste Management Division, Canada.
- King F, Kolar M, 2006.** Consequences of microbial activity for corrosion of copper used fuel containers – analyses using the CCM-MIC.0.1 code. Report 06819-REP-01300-00120-R00, Ontario Power Generation, Nuclear Waste Management Division, Canada.
- King F, Ahonen L, Taxén C, Vuorinen U, Werme L, 2001.** Copper corrosion under expected conditions in a deep geologic repository. SKB TR-01-23, Svensk Kärnbränslehantering AB.
- King F, Kolar M, Maak P, 2008.** Reactive-transport model for the prediction of the uniform corrosion behaviour of copper used fuel containers. *Journal of Nuclear Materials*, 379, pp 133–141.
- King F, Lilja C, Pedersen K, Pitkänen P, Vähänen M, 2010.** An update of the state-of-the-art report on the corrosion of copper under expected conditions in a deep geologic repository. SKB TR-10-67, Svensk Kärnbränslehantering AB.
- Kinnunen P, 2006.** Stress corrosion cracking investigations of copper in groundwater with acetate ions. Posiva Working Report 2006-18, Posiva Oy, Finland.
- LaGraff J R, Gewirth A A, 1995.** In-situ observation of oxygen adlayer formation on Cu(110) electrode surfaces. *Surface Science*, 326, pp L461–L466.
- Litke C D, Ikeda B M, 2006.** The effect of acetate concentration, chloride concentration, and applied current on stress corrosion cracking of OFP copper. Report 06819-REP-01300-10005, Ontario Power Generation, Nuclear Waste Management Division, Canada.
- Litke C D, Ikeda B M, 2008.** The stress corrosion cracking behaviour of copper in acetate solutions. NWMO TR-2008-21, Nuclear Waste Management Organization, Canada.
- Lu Z, Shoji T, 2006.** Unified interpretation of crack growth rates of Ni-base alloys in LWR environments. *Journal of Pressure Vessel Technology*, 128, pp 318–327.
- Lynch S P, 2007.** Progress towards understanding mechanisms of hydrogen embrittlement and stress corrosion cracking. CORROSION/2007, paper no. 489 [and citations therein]. Houston, TX: NACE International.
- Maak P, King F, 2005.** A model for predicting stress corrosion cracking of copper containers in a deep geologic repository. In: Van Iseghem P (ed). *Scientific basis for nuclear waste management XXIX*. Warrendale, PA: Materials Research Society. (Materials Research Society Symposium Proceedings 932), pp 837–844.
- Martins M E, Salvarezza R C, Arvia A J, 1996.** A comparative study of the early stages of mercury, cadmium, lead, silver and copper electrodeposition on columnar and smooth platinum electrodes. *Electrochimica Acta*, 41, pp 2441–2449.
- Masurat P, Eriksson S, Pedersen K, 2010.** Evidence for indigenous sulphate-reducing bacteria in commercial Wyoming bentonite MX-80. *Applied Clay Science*, 47, pp 51–57.
- McMurry J, Dixon D A, Garroni J D, Ikeda B M, Stroes-Gascoyne S, Baumgartner P, Melnyk T W, 2003.** Evolution of a Canadian deep geologic repository: base scenario. Report 06819-REP-01200-10092, Ontario Power Generation, Nuclear Waste Management Division, Canada.
- Meletis E I, Lian K, 1995.** Vacancy/dislocation interaction mechanism of transgranular stress corrosion crack. *Journal of the Mechanical Behavior of Materials*, 6, pp 69–84.

- Mori G, Scherer D, Schwentenwein S, Warbichler P, 2005.** Intergranular stress corrosion cracking of copper in nitrite solutions. *Corrosion Science*, 47, pp 2099–2124.
- Nabarro F R N, 1948.** Report on Conference on Strength of Solids. London: Physical Society, p 75.
- Newman R C, 2002.** Stress corrosion cracking mechanisms. In: Marcus P, Oudar J (eds). *Corrosion mechanisms in theory and practice*. 2nd ed. New York: Marcel Dekker, pp 399–450.
- Newman R C, Burstein G T, 1980.** Anion effects in the stress-corrosion cracking of copper and brass. *Journal of the Electrochemical Society*, 127, p 2527.
- Newman R C, Saito M, 1993.** Anodic stress-corrosion cracking – slip-dissolution and film-induced cleavage. In: Magnin T, Gras J M (eds). *Corrosion-deformation interactions*. Les Ulis: Les Editions de Physique, pp 3–26.
- Newman R C, Senior N A, 2010.** A revised interpretation of ultra-fast stress corrosion cracking experiments by Serebrinsky and Galvele. *Corrosion Science*, 52, pp 1541–1544.
- Newman R C, Sieradzki K, 1987.** Film-induced cleavage during stress-corrosion cracking of ductile metals and alloys. In: Latanision R M, Jones R H (eds). *Chemistry and physics of fracture*. Dordrecht: Nijhoff, pp 597–606.
- Newman R C, Zheng W, Procter R P M, 1992.** Stress corrosion cracking of C-Mn steels in methanol-ammonia environments. II. Electrochemical and fractographic studies. *Corrosion Science*, 33, pp 1033–1051.
- Parkins R N, 1976.** Mechanism of stress corrosion cracking. In: Shreir L L (ed). *Corrosion*. 2nd ed. London: Newnes-Butterworths, chapter 8.1.
- Pedersen K, 2000.** Microbial processes in radioactive waste disposal. SBK TR-00-04, Svensk Kärnbränslehantering AB.
- Pednekar S P, Agrawal A K, Chaung H E, Staehle R W, 1979.** Transgranular cracking of copper in 1M NaNO₂ solution. *Journal of the Electrochemical Society*, 126, pp 701–702.
- Petit J, Dequiedt J L, 2006.** Constitutive relations for copper under shock wave loading: twinning activation. *Mechanics of Materials*, 38, pp 173–185.
- Porath D, Bar-Sadeh E, Wolovelsky M, Grayevsky A, Goldstein Y, Millo O, 1995.** Annealing study of gold films using scanning tunneling microscopy. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, 13, pp 1165–1170.
- Pourbaix M, 1974.** Atlas of electrochemical equilibria in aqueous solutions. 2nd ed. Houston, Texas: National Association of Corrosion Engineers.
- Procter R P M, Omideyi M V E, Newman R C, Zheng W, 1992.** Stress-corrosion cracking of C-Mn steels in methanol-ammonia environments. I. Effects of environmental and mechanical variables. *Corrosion Science*, 33, pp 1009–1031.
- Pugh E N, 1979.** The stress-corrosion cracking of copper alloys. In: Arup H, Parkins R N (eds). *Stress corrosion research*. Alphen aan den Rijn: Sijhoff & Noordhoff, pp 177–208.
- Pugh E N, 1985.** Progress toward understanding the stress corrosion problem. *Corrosion*, 41, pp 517–526.
- Pugh E N, Montague W G, Westwood A R C, 1966.** Stress-corrosion cracking of copper. *Corrosion Science*, 6, pp 345–346.
- Puigdomenech I, Ambrosi J-P, Eisenlohr L, Lartigue J-E, Banwart S A, Bateman K, Milodowski A E, West J M, Griffault L, Gustafsson E, Hama K, Yoshida H, Kotelnikova S, Pedersen K, Michaud V, Trotignon L, Rivas Perez J, Tullborg E-L, 2001.** O₂ depletion in granitic media. The REX project. SKB TR-01-05, Svensk Kärnbränslehantering AB.
- Raj R, 1978.** Nucleation of cavities at second phase particles in grain boundaries. *Acta Metallurgica*, 26, pp 995–1006.
- Robert S, Gauthier S, Bocquet F, Rousset S, Duvault J L, Klein J, 1996.** An STM study of the adsorption of Pb on Cu(100): formation of an ordered surface alloy. *Surface Science*, 350, pp 136–144.

- Saito M, Smith G S, Newman R C, 1993.** Testing the film-induced cleavage model of stress-corrosion cracking. *Corrosion Science*, 35, pp 411–417.
- Schwentenwein S, Mori G K, Zitter H, 2002.** Stress corrosion cracking of semi-hard DHP-copper tubes in potassium nitrite solution. *CORROSION/2002*, paper 02432. Houston, TX: NACE International.
- Serebrinsky S A, Galvele J R, 2004.** Effect of the strain rate on stress corrosion crack velocities in face-centred cubic alloys. A mechanistic interpretation. *Corrosion Science*, 46, pp 591–612.
- Serebrinsky S A, Duffó G S, Galvele J R, 1999.** Effect of strain rate on stress corrosion crack velocity: difference between intergranular and transgranular cracking. *Corrosion Science*, 41, pp 191–195.
- Shahrabi T, Newman R C, 1989.** De-alloying and stress-corrosion cracking of copper alloys in cuprous ion solutions. In: Elsener B (ed). *Electrochemical methods in corrosion research III*. Zurich: Trans Tech, pp 169–176.
- Shahrabi T, Newman R C, Sieradzki K, 1993.** Stress-corrosion cracking of alpha-brass without copper oxidation. *Journal of the Electrochemical Society*, 140, pp 348–352.
- Shirai H, Nakano M, Hirose K, Sanada T, 1982.** Stress corrosion cracking of insulated wire for overhead distribution line and its prevention. *Dainichi-Nippon Cables Review*, 68, pp 62–71.
- Sieradzki K, Friedersdorf F J, 1994.** Notes on the surface mobility mechanism of stress-corrosion cracking. *Corrosion Science*, 36, pp 669–675.
- Sieradzki K, Kim J S, 1992.** Etch pitting and stress-corrosion cracking of copper. *Acta Metallurgica et Materialia*, 40, pp 625–635.
- Sieradzki K, Newman R C, 1985.** Brittle behaviour of ductile metals during stress-corrosion cracking. *Philosophical Magazine A*, 51, pp 95–132.
- Sieradzki K, Newman R C, 1987.** Stress-corrosion cracking. *Journal of Physics and Chemistry of Solids*, 48, pp 1101–1113.
- Sieradzki K, Sabatini R L, Newman R C, 1984.** Stress-corrosion cracking of copper single crystals. *Metallurgical and Materials Transactions A*, 15, pp 1941–1946.
- Sieradzki K, Kim J S, Cole A T, Newman R C, 1987.** The relationship between dealloying and transgranular stress-corrosion cracking of Cu-Zn and Cu-Al alloys. *Journal of the Electrochemical Society*, 134, pp 1635–1639.
- SKB, 2006.** Long-term safety for KBS-3 repositories at Forsmark and Laxemar – a first evaluation. Main report of the SR-Can project. SKB TR-06-09, Svensk Kärnbränslehantering AB.
- Smith J M, 2007.** The corrosion and electrochemistry of copper in aqueous, anoxic sulphide solutions. PhD thesis, University of Western Ontario.
- Stumpf R, Feibelman P J, 1996.** Towards an understanding of liquid-metal embrittlement: Energetics of Ga on Al surfaces. *Physical Review B*, 54, pp 5145–5150.
- Suzuki Y, Hisamatsu Y, 1981.** Stress corrosion cracking of pure copper in dilute ammoniacal solution. *Corrosion Science*, 21, pp 353–368.
- Szakálos P, Hultquist G, Wikmark G, 2007.** Corrosion of copper by water. *Electrochemical and Solid-State Letters*, 10, pp C63–C67.
- Taniguchi N, Kawasaki M, 2008.** Influence of sulfide concentration on the corrosion behaviour of pure copper in synthetic seawater. *Journal of Nuclear Materials*, 379, pp 154–161.
- Tersoff J, 1995.** Surface-confined alloy formation in immiscible systems. *Physical Review Letters*, 74, pp 434–437.
- Thompson D H, Tracy A W, 1949.** Influence of composition on the stress-corrosion cracking of some copper-base alloys. *Transactions of the American Institute of Mining, Metallurgical and Petroleum Engineers*, 1949, pp 100–109.

- Trevor D J, Chidsey C E D, 1991.** Room temperature surface diffusion mechanisms observed by scanning tunneling microscopy. *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures*, 9, pp 964–968.
- Uchida H, Inoue S, Koyama M, Morii M, K Koterazawa, 1991.** Susceptibility to stress corrosion cracking of pure copper in NaNO_2 solutions. *Zairyo*, 40, pp 1073–1078.
- Vasiljevic N, Dimitrov N, Sieradzki K, 2006.** Pattern organization on Cu(111) in perchlorate solutions. *Journal of Electroanalytical Chemistry*, 595, pp 60–70.
- Weissmüller J, Newman R C, Jin H-J, Hodge A M, Kysar J W, 2009.** Nanoporous metals by alloy corrosion: formation and mechanical properties. *Materials Research Society Bulletin* 34, pp 577–586.
- Yu J, Parkins R N, 1987.** Stress corrosion crack propagation in α -brass and copper exposed to sodium nitrite solutions. *Corrosion Science*, 27, pp 159–182.
- Zurek A K, 1987.** Brittle cracks in intrinsically ductile copper. *Scripta metallurgica*, 21, pp 1619–1622.

Analysis of the published discussions of the Surface Mobility Model (SMM)

We refer to the following discussion papers with the indicated abbreviations,

Sieradzki K, Friedersdorf F J, 1994. Notes on the surface mobility mechanism of stress-corrosion cracking. *Corrosion Science*, 36, pp 669–675. (SF94)

Galvele J R, 1994. Comments on “notes on the surface mobility mechanism of stress-corrosion cracking”, by K. Sieradzki and F.J. Friedersdorf. *Corrosion Science*, 36, pp 901–910. (GV94)

Gutman E M, 2003. Notes on the discussion concerning the “surface mobility mechanism” of stress corrosion cracking. *Corrosion Science*, 45, pp 2105–2117. (GT03)

Galvele J R, 2003. Reply to “Notes on the discussion concerning ‘surface mobility mechanism’ of stress corrosion cracking” by E.M. Gutman. *Corrosion Science*, 45, pp 2119–2128. (GV03)

Gutman E M, 2004. Comments on the “Stress corrosion cracking of zirconium and zircaloy-4 in halide aqueous solutions” by S.B. Farina, G.S. Duffo, J.R. Galvele. *Corrosion Science*, 46, pp 1801–1806. (GT04)

Galvele J R, 2004. Reply to E.M. Gutman’s: “comments on the “stress corrosion cracking of zirconium and Zircaloy-4 in halide aqueous solutions” by S.B. Farina, G.S. Duffo, J.R. Galvele”. *Corrosion Science*, 46, pp 1807–1812. (GV04)

The main points raised by SF94 have already been discussed – they are:

- The SMM uses the wrong expression for the change in vacancy formation energy due to stress; the expression used is appropriate for the interior of the solid, not the crack tip surface.
- The SMM does not take into account capillary effects that would close up very sharp cracks.

There are also detailed but important points of difference such as the necessity of using chemical potentials for the analysis.

In reply, GV94 raises the following points in rebuttal (we note that the chemical potential discussion is never taken up) –

SF94 did not take into account papers published subsequent to the original 1987 Galvele paper that introduced the SMM.

Galvele refers to a discussion with Oriani embedded in the 1988 Kohler conference proceedings /Duffo and Galvele 1990/, a paper submitted to the 1991 Parkins conference /Galvele 1992/, and a paper presented at the 1992 UMIST conference /Galvele 1993/. The last one might be considered an accessible peer-reviewed publication, although unknown to SF94 in June 1993 when they submitted their discussion. The first 8 pages are about other SCC mechanisms, the remainder is about the SMM. We have not found any information in this paper that answers the two principal criticisms by SF94. However the discussion of the origin of vacancies and vacancy formation energies is expanded, and a little different, acknowledging that the sa^3 term is for bulk metal – this was not at all clear in the 1987 paper /Galvele 1987/. So we can conclude that at this stage, Galvele was prepared to move the sink for the vacancies a little ahead of the crack so that bulk energetics could be applied, perhaps realizing that this was the only way to save the basic postulate of the model. There is nothing in the 1993 paper about capillary effects /Galvele 1993/.

It is interesting that the moving of the vacancy sink ahead of the crack turns the SMM into a *vacancy injection* model, qualitatively similar to those proposed by other authors including the late Denny Jones /Jones et al. 1997, Meletis and Lian 1995/. In those models the enhancement by stress of equilibrium vacancy concentration inside the solid was not taken into account – at least not explicitly – although it was probably part of the thought process.

SF94 wrongly assumed that Galvele was calculating what he thought was an equilibrium vacancy concentration on a surface, when such an equilibrium is not present owing to the occurrence of ongoing corrosion; the only place where one should assume equilibrium is inside the bulk solid ahead of the crack (just ahead, for Galvele's 'atomically sharp' crack). [our emphasis]

SF94 were deriving what they thought was a more appropriate version of the SMM, and probably never even considered that Galvele might believe the vacancies were finding their sink **ahead** of the crack, because this was not clear in the 1987 paper /Galvele 1987/, and requires an extra diffusion process that was not considered at all in 1987 (nor really in 1993 – it was just assumed to be possible). True, SF94's reformulation of the SMM might be quantitatively in error for a corroding metal, to the extent that vacancy concentrations on the free surface might be non-equilibrium.

SF94 focused on certain literature and derived or rederived certain results, but not the appropriate ones.

Again, the same point. Galvele is further defending the use of sa^3 and saying that considerations of equilibrium vacancy concentrations at a **surface** are irrelevant.

SF94 inappropriately analyzed the effect of a compressive stress on the behaviour of a crack. [our emphasis]

They are using some results that were derived for compression, but this does not appear to affect the validity of their approach.

SF94 ignore the crystalline nature of the solid.

To ignore this appears appropriate for order of magnitude estimation, especially when the analysis gives a steady state tip radius, during crack growth by their revised SMM, of the order of microns. We have to consider the context of SF94's analysis – they were not trying to understand how they thought SCC cracks grow – they were examining the limits of what a SMM might predict. Galvele's response starts by assuming that the sharp crack assumption is correct, then says it should be considered in any revised model. In reality it is Galvele who could be stretching continuum approaches beyond their reasonable limit, by postulating an atomically sharp crack and then guessing the change in vacancy formation energy a few atom spacings ahead of such a crack – not to mention that continuum mechanics does not predict such sharp cracks in metals.

SF94 ignore surface contamination and the stresses induced by corrosion products, including corrosion product wedging.

In SF94's presentation of a possible revised SMM, surface contamination would change the crack-flank interfacial energy and the surface diffusivity, but would still not produce realistic crack velocities, as discussed in the body of this report. They do assume equilibrium vacancy concentrations on the surface, and this has already been addressed.

Formation of 3D corrosion product phases, and the changes in local stress thus induced, appear – if anything – to argue against the SMM. First, such layers isolate the metal from the environment; second, they reduce the tensile stress ahead of the crack tip (except dealloyed layers, and except for the special case of wedging), which needs to be extremely high for the SMM to operate, at least in certain systems. Wedging can only occur if the crack angle is extremely low – which according to SF94 it isn't – so why should they have considered wedging? Because the SMM assumptions are right, in defiance of conventional mechanics of metals?!

SF94 say that a sharp crack would close up under capillary forces, but this cannot happen in the presence of corrosion products.

3D corrosion products are incidental in the SMM, and – as an aside – make it hard to see how it could operate (since the analysis is in terms of vacancies on the metal surface flowing to a site in or on the metal, somewhere near or at the crack tip). There is nothing in the model about corrosion products, only 'contamination', which one may assume is of a 2D character, following /Delamare and Rhead 1971/. This introduction of corrosion products seems to be a circular argument on Galvele's part – SCC is due to surface mobility, real cracks don't close up, therefore SF94's objec-

tion to the SMM on capillary grounds is invalid! But the argument as to the validity of the SMM has nothing to do with 3D corrosion products.

SF94's entire analysis is wrong because it assumes thermodynamic equilibrium and is thus only appropriate for a metal in contact with a completely inert environment.

The rebuttals become repetitive at this point. The same criticism of SF94 is restated for at least the fourth time. But it does come with an extra assertion, which is that the SMM would cease to apply altogether in an inert environment. This is an interesting point for SKB – Galvele himself is saying that cracking will not occur at all in an inert environment. Certainly it would be slow, but even SF94 estimate some finite crack velocity. We believe his statement on this point is incorrect.

SCC cracks are atomically sharp, therefore the maximum stress is within a couple of atom spacings of the crack tip, therefore *an exchange of vacancies with the crack tip could not be discarded* [our emphasis].

We do not believe SCC cracks are atomically sharp; neither do any mechanics experts that we know. It is true that SCC cracks are sharper than people used to think, and that is an active area of research. But if Galvele is only prepared to say that *an exchange with the crack tip could not be discarded* for a crack that is truly atomically sharp, how rapid is such an exchange for a crack, growing at ambient temperature, that has a believable tip radius of, say, 5–10 nm?

Such obfuscations were behind SF94's pardonable confusion as to where Galvele was placing his stress, and thus maximum equilibrium vacancy concentration.

So, in the course of the rebuttal, Galvele justifies the exchange of atoms [vacancies] between the surface and the applicable site **ahead** of the crack (required for the sa^3 assumption to be appropriate), but also makes some statements that appear contradictory –

Sieradzki and Friedersdorf started their work by saying that I followed Nabarro and Herring's reasoning to develop the equation for crack velocity V_p . As I pointed out in the discussion with Oriani² the reference to Nabarro and Herring was incidental, as it was used to obtain the equation for vacancy concentration in function of stress, for the metal at the tip of the crack, not for the surface of the crack. At the UMIST conference,⁴ in view of the confusions created by the previous reference, I repeated the development of the same equations based on the work of Hirth and Nix,⁵ which, incidentally, was published in the same Acta Metallurgica issue as the work by Larche and Cahn⁶ used in Sieradzki and Friedersdorf's work. I preferred the former one because it dealt with vacancy concentration in a volume, and, as I will show later, it is more appropriate to our mechanism than the equations developed by Larche and Cahn.

There is no mention whatsoever in my paper of any calculation of the vacancy concentration of the stressed surface. To avoid the effect of the environment I had to start the analysis of the system a few atomic layers below the surface.

To develop the SCC mechanism I have chosen to refer to Hirth and Nix,⁵ because their paper dealt explicitly with the case of vacancies in a stressed solid, and because they made explicit reference to the induction time necessary to reach the equilibrium vacancy concentration: a very important point for our mechanism, but not frequently found in the literature on the matter.

2: The temperature at which SCC takes place is lower than $0.5 T_m$. T_m is the absolute melting temperature for the metal or alloy considered. This postulate is supported by the available SCC data. The main consequence of this postulate is that volume diffusion in the metal, can be ignored.

4: SCC takes place by capture of vacancies by the tip of the crack. The capture of a vacancy, at the tip of the crack, leads to the propagation of the crack by an atomic step, and to a partial relaxation of the stressed lattice. Consequently, as a result of this step, there is a reduction in the free energy of the system. The capture of a vacancy by the stressed lattice at the tip of the crack, is the elementary step in the SCC process.

Since in our mechanism, the temperature is lower than $0.5 T_m$, the value for D is very low, and consequently the relaxation time very long. As a result of this, a vacancy deficient zone will be present at the tip of the crack.

We believe that the stress corrosion cracks are atomically sharp. This is sustained by the observations made by Silcock and Swann²³ for AISI Type 316 stainless steel exposed to a 42% $MgCl_2$ solution at 150°C. These authors observed cracks more than 10 μm long, with a cross section of only 10 nm. Such a low cross section allowed for very few events of slip emergence and dissolution, to keep such a high aspect ratio. For high stress intensities, 50 nm cracks were observed. From these observations it is reasonable to assume that the tip of the crack reaches atomic size distances. Consequently, the maximum stress value, in the x axis, should be found after a couple of atomic distances from the tip surface of the crack, and an exchange with the crack surface could not be discarded. This allows for the hydrostatic stress required in equation [2].

It is reasonable to assume that the environment by increasing the surface self-diffusion of the metal,² will also facilitate the atomic exchange between the surface and the first few atomic layers in the metal lattice. Taking into account the description they made for the action of the environment, Sieradzki and Friedersdorf cannot make any objection to the above assumption.

We do not consider this to be a self-consistent or clear set of arguments, particularly the comments that ‘volume diffusion can be ignored’ and the mention of a ‘vacancy deficient zone’ ahead of the crack. If it is vacancy deficient, because the vacancies cannot be transported fast enough – or at all – from the crack surface, then the concrete predictions of the SMM are incorrect, as they stand. As we understand the SMM, the rate-determining step is the movement of vacancies along the crack flank. Capture by the crack tip is supposed to be rapid.

The diffusion distance L along the crack flank, used to create a steady-state diffusion boundary condition in the SMM, is considered to be around 10^{-8} m. To state that this solid-liquid interfacial diffusion can be rate limiting when vacancies also have to diffuse a short distance in the solid (say, 10^{-9} to 10^{-8} m – we believe even the latter could be an underestimate for well-loaded cracks) is equivalent to saying that the self-diffusivity in the solid (albeit that the lattice is dilated by the high local stress) is **at most** one order of magnitude lower than that along the solid-liquid interface, *which is supposed to be highly enhanced by the environment in favourable cases of SCC!* This does not seem reasonable.

Criticisms by GT03

The following points are made –

1. Galvele is appealing to **volume processes** when the SMM is supposed to be a surface mobility model. Also, the applicable stresses in the applicable published analyses – e.g. for internal cavities – are normal to the cavity surfaces, but at the crack tip such a stress must be zero.
2. If we have understood correctly, Gutman casts doubt on the idea that there can be any steady vacancy flux, and thus crack growth rate, when both the crack flank and (stressed) crack tip have equilibrium vacancy concentrations. Equilibrium is equilibrium.
3. Accordingly, chemical potentials should be used, not concentrations.
4. Gutman highlights the internally contradictory nature of the quoted passages from GV94 already given. Is diffusion supposed to be on the surface or in the lattice?
5. Gutman doubts the atomically sharp crack assumption and mentions some findings of elastic-plastic fracture mechanics.
6. Gutman discusses the parameter L (diffusion distance along the crack flank) and cites some niceties of electrode kinetic theory.
7. The consistency between the SMM and the measured crack velocities, especially the applicable activation energies for crack growth, is questioned.
8. The potential dependence of SCC velocity is considered to be inconsistent with the rate determining diffusion process assumed in the SMM, and anyway to be impossible on IR-drop grounds, were the cracks to be as sharp as assumed in the SMM.

This is quite a lot of objections to the SMM. In considering the response in GV03, we consider only some highlights that make some continuity with the earlier discussion around the criticisms of SF94. Points 6–8 are not considered further, and anyway are not easy to resolve completely.

So, in GV03, we find the following – we have had to cut and paste, rather than quote or paraphrase, in order to capture certain examples of the reasoning –

What Gutman avoids to mention is that Sieradzki and Friedersdorf [3] concluded that the SMM was correct, but that it overestimated the crack propagation rate (CPR) values by about 14 orders of magnitude. To reach this last conclusion they erroneously calculated the surface vacancy concentrations with equations developed for metals in the absence of a corrosive environment, and also had to assume that the crack tip diameters were of the order of $10\ \mu\text{m}$, when the values reported in the literature were less than $10\ \text{nm}$ [4]. I will return to the point of the crack tip diameter at the end of the present discussion, as it was done in the notes.

This is stretching the word ‘correct’ to breaking point! SF94 had to change the location of the operable stress, use chemical potentials rather than concentrations, and introduce capillary forces to obtain what they considered a ‘correct’ SMM.

Before going any further in this discussion it is important to recall a point that is frequently ignored by our critics. The SMM is based on four postulates [5,6]. There is nothing wrong if any of our critics decides to choose other postulates, and develops a different mechanism. What is not correct for our critics is to suggest that we should introduce changes in our equations that would contradict the postulates of our mechanism. This type of suggestion is found in various parts of the notes.

No comment.

Gutman asks if the SMM is based on surface diffusion or on volume diffusion. The surfaces in metals are not geometrical surfaces of zero thickness. Computer simulation studies show that the concentration of vacancies in a metal is affected by a clean surface up to some four or five atomic layers. One could guess that in the presence of a contaminant that increases the surface mobility this effect could be extended to a few atomic layers more. In Ref. [1] we mentioned that the model assumes that there is an atomic exchange between the surface and the first few atomic layers.

This assumption was required to rescue the entire model from its use of the sa^3 term for the change in vacancy formation energy, which is only applicable to the bulk of the solid. The argument fails if cracks are not atomically sharp.

We also accept, as unquestionable, the statement that the value of $\sigma_{xx} = 0$ on the free surface at the tip of the crack. This is almost a matter of faith. But the work by Thomas and Bruemmer [21] should be mentioned. In Fig. 16 of their work these authors show a very good picture of the tip of a stress corrosion crack. In that picture we see an oxide film at the tip of the crack. In other words, the tip of the crack is not a free surface. As far as I know there is no information about the value of σ_{xx} on the metal surface, at the tip of the crack, under an oxide film. The problem of our general ignorance about what happens at a molecular level, at the tip of the crack, was one of the main conclusions of my lecture in Granada [22].

If the metal surface is truly covered by an adherent oxide, such that this stress can be large, then the SMM must fail anyway.

The notes strongly question the assumptions made about the crack tip diameter in all our papers related to SMM. It is suggested that we assumed atomically sharp cracks only to validate the SMM. To disqualify our assumptions, Gutman calculated the polarization required at the tip of the crack. To this purpose he quoted a paper he submitted at the Third I.C.C. in Moscow in 1966 [29]. In this paper Gutman developed a theoretical model for current distribution in a stress corrosion crack. In that model all the crack surface was in an active state and, for some obscure unexplained reason, a high anodic current circulated from the tip of the crack. In the notes, with small changes, Gutman reproduced the calculation he made in his 1966 paper. Gutman's conclusion, in the notes, is that the width at the tip of the crack is higher than 20,000 atomic sizes. If this calculation is applied to Ni ($a = 2.5 \times 10^{-10}$ m), Gutman's crack tip would have at least 5000 nm. This conclusion is in contradiction to what we find in the literature. For example Silcock and Swann [30] studied samples of AISI Type 316 stainless steel stress corroded in 42% MgCl₂ at about 150 °C, and found cracks with a width of less than 10 nm (i.e. about 40 atomic diameters). Another example is the work by Thomas and Bruemmer [21] where they showed, for SCC cracks developed in Ni alloys, crack tips of less than 10 nm. In conclusion, when we assumed that the crack tips were atomically sharp, it was not because it was required for the SMM, it was because that was the experimental evidence. Of course, if the crack tips were 5000 nm thick then the SMM would not be applicable. But this is not what we found in the literature.

There are strong doubts as to whether the dominant cracks that propagate at the rates Galvele uses in his correlations are as sharp as the cracks studied by Bruemmer and Thomas. These cracks susceptible to TEM study are likely side branches that are highly shielded by adjacent crack segments and have arrested or are propagating slowly. This is, however, an unresolved issue.

Even 10 nm seems much too far for vacancies to diffuse ahead of the crack, especially if they have to do so faster than they are diffusing on the crack flank! (Because this distance is similar to L in the model). Granted, the lattice is dilated ahead of the crack, but compared with a free surface with 'contamination' causing a radically enhanced surface diffusion kinetics?

How about SCC or LME processes that proceed at 10 or 100 microns/s? Or 20 mm/s as in Serebrinsky and Galvele? How does that work if the vacancy sink is 10 nm ahead of the crack?

Criticisms by GT04

Again we omit discussions of activation energies and electrochemical aspects in general. Again we are obliged by the complex nature of the arguments to quote directly.

#1

Further, “the applicability of several SCC mechanisms (anodic dissolution, hydrogen embrittlement, stress-sorption, film-induced cleavage and surface-mobility SCC mechanism) was evaluated in order to explain the experimental observations”.

Thus, a reader can expect the author of Ref. [1] to compare the results of cpr evaluation for each of the above-mentioned mechanisms with experimental results using expressions of (1) type. As for his surface-mobility mechanism (SMM) of SCC, the author gives an expression that he has described more than once in his papers

$$\text{cpr} = \frac{D_s}{L} \left[\exp \left(\frac{\sigma a^3}{kT} \right) - 1 \right], \quad (2)$$

where D_s is the surface self-diffusion coefficient; L is the diffusion path of the vacancies; σ is the elastic surface stress at the tip of a crack (which is approximated by the author as the yield strength of the material); a is the atom size; k is the Boltzmann constant, and T is the absolute temperature. However, he does not discuss any expressions for other mechanisms. Thus, on the one hand, he comes into conflict with his own declaration cited above, and on the other, discriminates other mechanisms in favor of SMM. Such an approach gives the impression that the author [1] merely continues imposing his SMM despite detailed discussions on the topic (e.g., [2,3]).

Excellent polemic, but not very helpful for our discussion – we include this to give a flavour of the extraordinary style of these articles.

#2

The next question arises when the author [1] explains the SCC stages: first, the slow stage of “intergranular cracking due to anodic dissolution assisted by stresses; then a transition from intergranular to transgranular cracking and rapid transgranular propagation”, the latter being explained by the author as SMM. However, by his own SMM logical reasoning, it should be just the opposite. Grain boundaries are contaminated with various impurities decreasing T_m (this fact is known in metallurgy), and according to SMM, the self-diffusion rate during IG cracking should be much higher than during TG cracking! So why does the anodic dissolution during IG cracking assisted by stresses make way to SMM at the transition from IG cracking to TG cracking, if the stress concentration and local plastic deformation rate in the crack tip grow with crack deepening, i.e. the driving force of stress-assisted anodic dissolution increases?

#3

The approach chosen for SMM is erroneous and primitive, which is evident from the following example. The problem of diffusion in a stress field (so called “uphill diffusion” or mechanodiffusion) is not completely solved as yet due to its complicated nature, although it has been studied for many years (e.g., in metallurgy). Note

that in the case of SCC problems it becomes even more complicated due to inhomogeneous and non-stationary stress field distribution in crack tips. By way of example, let us examine in a generalized and simplified form the effect of elastic stress gradient on diffusion, which makes the first Fick law insufficient [8].

.....

$$\frac{\partial C}{\partial t} = D \text{grad} \left(\text{grad} C + \frac{C \text{grad} U}{kT} \right). \quad (6)$$

The solution of this equation provides the concentration distribution $C(x, y, z, t)$ in time and space. Then, proceeding from $C(x, y, z, t)$, we can calculate the diffusion flux $J(x, y, z, t)$ in each spatial point using Eq. (4). Naturally, to solve these equations, we should specify, as usual, boundary and initial conditions for the given problem. The potential of the stress field represents the potential energy of an elastic interaction. For example, for a concentrated stress source it has the form of the Green function, etc. [9].

#4

$$\text{cpr} = \frac{D_S}{L} \frac{\sigma a^3}{kT}. \quad (7)$$

As pointed out in [11], “apart from the precise value of the numeral factor, which depends on the geometry of the model and the rigour of the calculation, *this is the Nabarro–Herring equation of vacancy creep*” presented in [12] as

$$\dot{\epsilon}L = \alpha \frac{D}{L} \frac{\sigma a^3}{kT}, \quad (8)$$

where the constant α is close to a unity [12], D is the coefficient of self-diffusion, $\dot{\epsilon}$ is the creep strain rate at the steady-state stage and $\dot{\epsilon}L$ is the creep deformation rate [13, p. 7], or presented in [11] as

$$\dot{\epsilon}L = 8 \frac{D}{L} \frac{\sigma a^3}{kT}, \quad (9)$$

presented in [13] as

$$\dot{\epsilon}L = 14 \frac{D}{L} \frac{\sigma a^3}{kT}, \quad (10)$$

etc.

The comparison of *right parts* in Eqs. (7)–(10) *reveals their identity* with the same physical meaning, and the author’s rushing between Nabarro–Herring or Hirth–Nix models [4,6,7] criticized earlier in my Notes [3] does not help. It is a phantom that a common creep deformation rate $\dot{\epsilon}L$ was called by Galvele “crack propagation rate” without any grounds. Consequently, a “good correlation” of calculated values of the creep deformation rate with measured values of the “crack propagation rate” points only to a low quality of the fitting [1], but cannot support SMM; it rather rejects it because this “good correlation” is related to absolutely different matters. Indeed, the creep deformation rate at a steady-state stage cannot be equal numerically to the crack propagation rate in any case. As is well known [14], in a common creep process the creep rate at the steady-state stage (secondary creep) is a period of constant creep rate called “minimum creep rate”, and it is much lower than on the final failure stage (tertiary creep) developed due to the formation of internal voids and cracking.

and

Concluding this analysis, it seems that the paper [1] gives no experimental evidence of SMM validity and confirms only the fact that SMM is built on a contradictory and erroneous basis. I think that even without the longstanding criticism of SMM, the illegitimate substitution of the usual creep deformation rate [Eqs. (8)–(10)] by the crack propagation rate [Eq. (7)] is a sufficient reason to reject SMM.

Responses in GV04

Stress assisted diffusion? There is no doubt that stress assisted, or stress induced, diffusion is a very important subject. One could mention, for example, the recently published work by Takahashi and Uesugi [10] on the bonding process of fine gold wires, at room temperature. After reading the work by Takahashi and Uesugi one does not get the impression that stress assisted vacancy diffusion is an unsolved problem, as suggested by Gutman in his comments.

But, the surface mobility SCC mechanism does not include stress assisted diffusion! The stresses that could be present on the walls of the cracks play, in the SMM, only a secondary role, and could never account for the wide range of crack propagation rates (CPR) found in SCC. Sieradzki and Friedersdorf [11] calculated the contribution of surface stresses to the CPR and concluded that it was insignificant.

We feel this is playing on words to some extent. Gutman delivers examples that are indeed ‘stress assisted diffusion’ in the purist sense, but he clearly does not miss the subtleties of what the SMM is. From one of his own papers /Galvele 1995/:

“Stress Distribution Heterogeneity: ...When the crack is observed from the inside of the material, there is a stress concentration induced by the presence of the crack. However, when the crack is observed from within the environment, a very important point is noticeable: the walls of the crack show practically no stress, while a very high stress concentration is found at the tip of the crack. From the point of view of stress distribution, the environment is in contact with a strongly heterogeneous material. The metal is practically stress-free, with a very high stress concentration located at the tip of the crack. Computer simulation of cracks [13] shows that this heterogeneity covers a very short distance, amounting only to several interatomic distances”.

Ref 13 must have dealt with a strong solid, not a metal which yields at the crack tip (or else the stress was very low) /deCelis et al. 1983/.

Since we are talking about the SMM and SCC, I will take the opportunity to make a side comment on this matter. When the SMM was first published, in 1987, [14] a full chapter was dedicated to *hydrogen embrittlement*. It was suggested that the presence of hydrogen would increase the concentration of vacancies, in the same way as stresses did in Eq. (1). To account for the effect of hydrogen on the CPR, the following equation was suggested:

$$\text{CPR} = \frac{D_s}{L} \left[\exp \left(\frac{\sigma a^3 + \alpha E_b}{kT} \right) - 1 \right] \quad (3)$$

where E_b was the binding energy for H-monovacancies, and α is a dimensionless function that measures the difference in degree of saturation with hydrogen of the vacancies, between the stressed and the stress-free regions. The value of α should range between 0 and 1, and will be function of stress.

In 1993 Fukai and Okuma discovered that the presence of hydrogen induced superabundant vacancies in metals [18,19]. This phenomenon was confirmed for titanium, chromium, aluminium, iron, manganese, cobalt, nickel, palladium, stainless steel, etc. This observation not only confirms the assumption made when developing Eq. (3), but it is also meant to call the attention of our SCC community, so strongly influenced by the “dislocations culture”.

This correlation (between hydrogen and vacancy generation) is of course mirrored or exceeded in importance by interactions of hydrogen with dislocation generation and motion, which are dynamic processes involved in crack growth.

In the 1987 paper [14] (page. 5), after developing Eq. (2), I said: At very low stress values, when $\sigma a^3 \ll kT$, Eq. (2) can be approximated by

$$\text{CPR} = \frac{D_s}{L} \frac{\sigma a^3}{kT} \quad (4)$$

Then, in the same paper, I calculated the range of validity of Eq. (4), which was shown in [14] (page. 6, Fig. 4). Eq. (4) was found to be valid only for σ values lower than 10 MPa. In all our papers, when we applied SMM we assumed that the value of σ was equal to the yield strength of the metal. In other words, since the σ values used were higher than the limit of validity of Eq. (4), we have never used this equation.

In his “comments” Gutman says that Eq. (4) has the same shape that the equations for high temperature creep. Consequently he concludes that we were using an equation for creep to calculate the crack propagation rates. As I said above, we never used Eq. (4), and I do not understand why Gutman made the statements he did.

This discussion remains to be completed. To the extent that the SMM uses the change in vacancy formation energy from Nabarro and Herring, but then assumes local stresses at or exceeding yield, various contradictions appear, including the atomistic sharpness of the crack. The two authors are arguing ‘past’ each other here, as in so many of these discussions. That is not to say that vacancies might not be involved in some slow SCC processes at ambient temperature, or relatively fast ones at 300 deg C. But fast ones at ambient, when the vacancies have to diffuse 10 nm in the solid? That is a real sticking point.

What we find unacceptable is the criticism for its own sake, and without alternative proposals. We would have expected our critics to have analysed why the SMM seemed to work, and would have given us a better explanation of the process. We will be the first to scrap the SMM as soon as we are confronted with a better mechanism.

Again, no comment.

References

- deCelis B, Argon A S, Yip S, 1983.** Molecular dynamics simulation of crack tip processes in alpha-iron and copper. *Journal of Applied Physics*, 54, pp 4864–4878.
- Delamare F, Rhead G E, 1971.** Increase in the surface self-diffusion of copper due to the chemisorption of halogens. *Surface Science*, 28, pp 267–284.
- Duffó G S, Galvele J R, 1990.** Surface-mobility stress corrosion cracking mechanism in silver alloys. In: Gangloff R P, Ives M B (eds). *Proceedings of the International Conference on Environment-Induced Cracking of Metals*, Kohler, Wisconsin, 2–7 October 1988. Houston, TX: NACE International, pp 261–264, and appended discussion between J.R. Galvele and R.A. Oriani.
- Galvele J R, 1987.** A stress corrosion cracking mechanism based on surface mobility. *Corrosion Science*, 27, pp 1–33.
- Galvele J R, 1992.** In: Bruemmer S M, Meletis E I, Jones R H, Gerberich W W, Ford F P, Staehle R W (eds). *Proceeding of the Parkins Symposium on Fundamental Aspects of Stress Corrosion Cracking*. Warrendale, PA: The Minerals, Metals and Materials Society, p 85. /bidragets titel saknas/
- Galvele J R, 1993.** Surface mobility mechanism of stress-corrosion cracking. *Corrosion Science*, 35, pp 419–434.
- Galvele J R, 1994.** Comments on “notes on the surface mobility mechanism of stress-corrosion cracking”, by K. Sieradzki and F.J. Friedersdorf. *Corrosion Science*, 36, pp 901–910. (GV94)
- Galvele J R, 1995.** Electrochemical aspects of stress corrosion cracking. In: Bockris J O’M, Conway B E, White R W (eds). *Modern aspects of electrochemistry*. No. 27. New York: Plenum Press, pp. 233–358.
- Galvele J R, 2003.** Reply to “Notes on the discussion concerning ‘surface mobility mechanism’ of stress corrosion cracking” by E.M. Gutman. *Corrosion Science*, 45, pp 2119–2128. (GV03)
- Galvele J R, 2004.** Reply to E.M. Gutman’s: “comments on the “stress corrosion cracking of zirconium and Zircaloy-4 in halide aqueous solutions” by S.B. Farina, G.S. Duffo, J.R. Galvele”. *Corrosion Science*, 46, pp 1807–1812. (GV04)
- Gutman E M, 2003.** Notes on the discussion concerning the “surface mobility mechanism” of stress corrosion cracking. *Corrosion Science*, 45, pp 2105–2117. (GT03)
- Gutman E M, 2004.** Comments on the “Stress corrosion cracking of zirconium and zircaloy-4 in halide aqueous solutions” by S.B. Farina, G.S. Duffo, J.R. Galvele. *Corrosion Science*, 46, pp 1801–1806. (GT04)
- Jones D A, Jankowski A F, Davidson G A, 1997.** Room-temperature diffusion in Cu/Ag thin-film couples caused by anodic dissolution. *Metallurgical and Materials Transactions A*, 28, pp 843–850.
- Meletis E I, Lian K, 1995.** Vacancy/dislocation interaction mechanism of transgranular stress corrosion crack. *Journal of the Mechanical Behavior of Materials*, 6, pp 69–84.
- Sieradzki K, Friedersdorf F J, 1994.** Notes on the surface mobility mechanism of stress-corrosion cracking. *Corrosion Science*, 36, pp 669–675. (SF94)

Surface mobility model as applied to SCC of copper and silver and their alloys in gaseous environments containing halogens

One of the cornerstones of the surface mobility model is the cracking observed by /Bianchi and Galvele 1993, 1994/ in copper and silver, and AgPd alloys, in various gaseous halogen atmospheres. Some of the temperatures were quite low, e.g. 200°C, versus melting points of the metal halides in the range 400 to 600°C. The seminal work of Gordon Rhead /Delamare and Rhead 1971/ on enhancement of surface self-diffusion of Cu by halogen adsorption was one of the chief stimuli for the initial development of the surface mobility model, and for this particular experimental work.

As usual, there are multiple alternative explanations for the data. In particular, one has to ask – why was SCC reported for pure copper in different halogen atmospheres, but for pure silver only in iodine? The work in bromine /Bianchi and Galvele 1994/ used a Pd-Ag alloy, not pure silver. Inspection of the literature shows that amongst the Cu and Ag halides, those that show ‘superionic’ conduction are CuCl, CuBr, CuI and AgI /Howells 1997, Takahashi 1978, Tankeshwar and Tosi 1991, Yashima et al. 2006/. AgBr is not a superionic conductor, or at least requires a temperature very close to its melting point to show such behaviour. So a very logical explanation of the data is that this is a kind of tarnish rupture mechanism in which a thick metal halide film grows down the grain boundaries by something akin to superionic conduction. This is not the same thing as enhanced surface mobility, although there may be superficial analogies. PdAg will be more susceptible in a less ionically conducting system (where the film formed is AgBr) because the crack tip zone is stronger and ‘sharper’ (nanoporous Pd layer embedded in AgBr, or vice versa) and triggers easier cracking.

Further reading on the surface science of halogen interactions is provided by /Baier et al. 2002, El'tsov et al. 1991, Giesen 2001, Nakakura and Altman 1998, 1999, Park et al. 1986, Sesselmann and Chuang 1986a, b, Sette et al. 1988, Walter et al. 1996/.

References

- Baier S, Dieluweit S, Giesen M, 2002.** Step and island dynamics on Cu(111), Ag(111) and Au(100) electrodes in electrolyte. *Surface Science*, 502–503, pp 463–473.
- Bianchi G L, Galvele J R, 1993.** Stress corrosion cracking of pure copper and pure silver in gaseous environments. *Corrosion Science*, 34, pp 1411–1417.
- Bianchi G L, Galvele J R, 1994.** Stress corrosion cracking of silver alloys in gaseous environments. Bromine vapour. *Corrosion Science*, 36, pp 611–619.
- Delamare F, Rhead G E, 1971.** Increase in the surface self-diffusion of copper due to the chemisorption of halogens. *Surface Science*, 28, pp 267–284.
- El'tsov K N, Zueva G Y, Klimov A N, Martynov V V, Prokhorov A M, 1991.** Reversible coverage-dependent $\text{Cu} + \text{Cl}_{\text{ads}} \rightarrow \text{CuCl}$ transition on Cu(111)/Cl₂ surface. *Surface Science*, 251–252, pp 753–758.
- Giesen M, 2001.** Step and island dynamics at solid/vacuum and solid/liquid interfaces. *Progress in Surface Science*, 68, pp 1–154.
- Howells W S, 1997.** Quasielastic neutron scattering in copper halides. *Physica B: Condensed Matter*, 241–243, pp 329–331.
- Nakakura C Y, Altman E I, 1998.** Scanning tunneling microscopy study of the reaction of Br₂ with Cu(100). *Surface Science*, 398, pp 281–300.
- Nakakura C Y, Altman E I, 1999.** Scanning tunneling microscopy study of halide nucleation, growth, and relaxation on singular and vicinal Cu surfaces. *Surface Science*, 424, pp 244–261.

- Park S, Rhodin T N, Rathburn LC, 1986.** Halide formation and etching of Cu thin films with Cl₂ and Br₂. *Journal of Vacuum Science & Technology A*, 4, pp 168–172.
- Sesselmann W, Chuang T J, 1986a.** The interaction of chlorine with copper: I. Adsorption and surface reaction. *Surface Science*, 176, pp 32–66.
- Sesselmann W, Chuang T J, 1986b.** The interaction of chlorine with copper: II. Bulk diffusion. *Surface Science*, 176, pp 67–90.
- Sette F, Hashizume T, Comin F, MacDowell A A, Citrin P H, 1988.** Coverage and chemical dependence of adsorbate-induced bond weakening in metal substrate surfaces. *Physical Review Letters*, 61, pp 1384–1387.
- Takahashi T, 1978.** Silver and copper ion conductors in the solid state. *Pure and Applied Chemistry*, 50, pp 1091–1098.
- Tankeshwar K, Tosi M P, 1991.** Ionic diffusion in superionic-conductor melts. *Journal of Physics: Condensed Matter*, 3, pp 7511–7518.
- Walter W K, Manolopoulos D E, Jones R G, 1996.** Chlorine adsorption and diffusion on Cu(111). *Surface Science*, 348, pp 115–132.
- Yashima M, Xu Q, Yoshiasa A, Wada S, 2006.** Crystal structure, electron density and diffusion path of the fast-ion conductor copper iodide CuI. *Journal of Material Chemistry*, 16, pp 4393–4396.