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Bi-modal trends in the long-term corrosion of copper and high copper alloys

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The evolution of corrosion loss and maximum pit depth of copper and copper alloys exposed for long periods of time in natural and industrial environments is shown to be more consistent with a bi-modal functional form than with the classical power law. Data from several long-term exposure test programs supports this proposition. The bi-modal behaviour signals a change from mainly cathodic oxygen reduction to a subsequent transitory corrosion process that may be modelled as involving pitting under earlier copper corrosion products. Possible reasons for some data sets showing decreasing maximum pit depths with increasing exposure time are discussed.

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- C. Crevice corrosion
- C. Pitting corrosion

1. Introduction

Copper and in particular high copper alloys such as copper nickels and certain brasses are used extensively in marine applications for piping, tubing, condensers and heat exchangers and, at one time, for sheathing the hulls of timber ships, largely because of their high resistance to corrosion and their good resistance to bio-fouling [1,2]. Copper as an exterior casing to a carbon steel lining has been proposed for containers for nuclear wastes buried in deep geological repositories and exposed to ground-waters [3]. Copper has a record of excellent corrosion resistance in atmospheric exposure conditions [4,5]. As a major component of bronzes, copper has a particularly long history of use in art [6] and is of much interest to archaeologists and museum curators [7].

There has been more than a century of scientific study of the corrosion of copper, particularly in relation to its behaviour in seawater and in sulphur dioxide contaminated atmospheres [5,6,8]. In chlo-ride environments early investigations [9,10] identified the corrosion products formed on copper to consist of mainly of cuprous oxide (Cu_2O), cuprous chloride (CuCl) as well as other products including cupric hydroxide $\text{Cu}(\text{OH})_2$, cupric oxide CuO and to a lesser extent, mainly in the outer layers of the corrosion product, the loosely adherent precipitation products atacamite ($\text{Cu}_2(\text{OH})_3\text{Cl}$) and malachite ($\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$) [11]. The dependence of these products on pH and electrochemical potential has been summarised in Pourbaix diagrams for the (Cu , H_2O , Cl^-) system [12,13] with inclusion also of carbonate and bicarbonate ions as necessary for

real seawaters (since these usually are carbonate–bicarbonate saturated). This pH dependence applies both for very short-term corrosion but also for longer term exposures. For example, compared to copper corrosion in 3%w/v NaCl solutions, the buffering capacity of seawater and the saturation of carbonates tend to lower the rate of Cu_2O production and to increase the production of cuprous complexes. The effect is to produce higher corrosion in (non-stagnant) seawater compared with simple saline solutions [14]. Also, for exposures up to about 90 days, there appeared to be negligible effect caused by the concentration of dissolved oxygen, which suggested that oxygen diffusion was not the rate-controlling mechanism for these exposure periods. On the other hand, there can be considerable differences in corrosion response between short term and long term exposures, for example as has been noted for 90:10 copper–nickels under the same environmental exposure conditions [15,16]. It follows that understanding of the corrosion behaviour of copper alloys for long-term service may not necessarily be available from short-term observations.

Long-term corrosion behaviour both for mass loss and for maximum pit depth as a function of exposure time is relevant for the estimation of future life or remaining life of infrastructure [17]. Traditionally, and particularly for atmospheric corrosion, it was assumed that the power law, derived originally by Tammann [4] in 1923 for copper roofs and used empirically for steels in 1934 [18] could be used to describe the progression of mass loss as a function of time, both for short-term (days, weeks) and for long-term (decades) exposures. However, already in 1968 Hummer et al. [19] observed the poor fit of the power law to data for longer-term corrosion of copper.

More recently it has been shown that in a variety of exposure conditions including marine, freshwater and various atmospheric environments the data for corrosion loss (and also maximum pit depth) typically follows a characteristic bi-modal functional form (Fig. 1). This has been found to be the case for a variety of steel types including low-alloy and copper-bearing steels, weathering steels and the more common grades of chromium-bearing or stainless steels [20]. It also applies to cast iron [21] and recently has been shown to apply also for corrosion loss and for maximum pit depth for a variety of aluminium alloys [22]. The bi-model functional form has been modelled as a sequence of consecutive phases, each representing a corrosion rate controlling process. They are shown in Fig. 1. The main parameters that describe each phase have been calibrated to field data for low-alloy and copper-bearing steels continuously immersed in normal, unpolluted coastal seawater [20]. The effects of various environmental parameters including nitrogenous water pollutants [23] have been considered.

The present paper is concerned with the extent to which the bi-modal trend is valid for the corrosion of copper and high copper alloys in long-term exposures, mainly in marine exposure conditions and also in some other natural and industrial environments. As in the earlier work, the analysis proceeds with the working hypothesis that the bi-modal function is applicable. This means that it is assumed that the underlying physico-chemical processes governing corrosion are assumed given, in conceptual form (see Fig. 1), and must be calibrated to suitable and relevant data. Corrosion observations that form the data items should be considered samples from the underlying physico-chemical processes and as such are prone to uncertainty. In some cases it is possible for the data to be in error. Importantly, the data themselves are but part of the information available. They do not by themselves define the model. Therefore an approach based on curve-fitting to determine a model is considered not acceptable. On the contrary, the present approach permits the introduction of prior knowledge and of understanding of the development of the corrosion process and the effect of corrosion products on the diffusion processes involved in that process [20]. An important part of this is the knowledge that some other metals and alloys already have been shown to follow the bi-modal functional form.

In the next section data reported in the literature for copper corrosion loss are used and where necessary re-interpreted to show that for marine immersion, tidal, marine coastal, fresh water and inland atmospheric corrosion environments and some industrial environments the bi-modal model is appropriate in the majority of cases. The same approach is taken for the very limited data available for pitting corrosion. The reasons for the persistent observation of the bi-modal trend are then discussed. Attention is given also to why the bi-modal behaviour is (almost) absent in the case

of (commercially) pure copper in fresh water with very low ion contents and also in some atmospheric exposure environments. Finally, an explanation is proposed for the apparently anomalous observations that for pitting in some cases the maximum depth of pitting appears to reduce with increasing exposure period.

2. Corrosion loss data and trends

2.1. Data sources

Most investigations of the corrosion behaviour of copper and copper alloys have focused on short-term laboratory trials, electrochemical testing, examination of corrosion products, or relatively short field exposure programs [8,24], [25]. There are some exceptions, including the 20 year study of atmospheric corrosion for a range of almost pure coppers from various manufacturers exposed to 3 different atmospheric environments [26,27]. In this test program, commenced in 1932, the total coupon mass, including corrosion products was measured at 1, 2, 3 and 5, and the mass of cleaned coupons only at 8, 10 and 20 years exposure. Using the assumption that all copper lost to corrosion was converted to corrosion product (Cu_2O) and thus included in the measured mass, produced, after allowing for the relative molecular masses, overestimates of the loss of metal for years 1, 2, 3 and 5. More difficult was the data for the test program of various copper alloys [28,29] apparently commenced in 1927. In this test program, the total coupon mass, including corrosion products was measured at 1, 2, 3, 5, 8 and 10 years, and the mass of cleaned coupons only at 10 and 20 years exposure. Because some coupons showed mass increases (as a result of corrosion product) and since it is not known how much of the metal loss was lost to the environment rather than being converted into adherent corrosion product, it was found not possible to derive reasonably accurate estimates of metal mass loss from the results reported for 1, 2, 3, 5 and 8 years exposure. As a result, this data was disregarded. Another long-term test program [30] for the atmospheric corrosion of copper alloys took observations only at a small number of points in time, insufficient for use herein. The most extensive set of corrosion loss and pit depth data for copper and copper based alloys was found to be those obtained in the 16 year exposure experiments in the Panama Canal Zone (PCZ) conducted in the period just after the Second World War when it was realised that there was very little data for corrosion in tropical climates [19,31]. In this work observations were made at 1, 2, 4, 8 and 16 years of exposure from which mass loss, maximum pit depth and the average of the 20 deepest pits (from 4 faces of duplicate coupons) were derived. This program also reported data for a variety of copper alloys. Table 1 summarises the alloys considered herein and Table 2 the exposure conditions.

Fig. 1. Bi-modal corrosion loss model showing phases 0–4 with a summary description for each, together with the parameter t_a dividing the predominantly aerated (oxic) mode (phases 0–2) from the predominantly de-aerated (anoxic) mode (phases 3 and 4). The instantaneous corrosion rate r_b near the end of phase 2 and just before reaching t_a changes to r_a thereafter, that is, near the beginning of phase 3.

Table 1

Summary of composition of some copper alloys (% by weight).

Alloy	Refs.	Cu	Zn	Mn	P	S	Si	Fe	Al	Sn	Pb	Ni
Copper	[19]	99.92–99.94	–					–				
Silicon bronze	[19]	95.30–96.14	<0.54	<0.08			2.64–2.90	0.04–0.05				
Phosphor bronze	[19]	95.10–95.54	<0.30	<0.07	0.25–0.36			0.01–0.04		4.21–4.38	<0.05	
Aluminium bronze	[19]	94.84–95.68	<0.01					0.03–0.08	3.77–5.07		<0.01	<0.05
Commercial bronze	[19]	80.7–90.5	9.5–10.3					<0.01			<0.03	
90:10 Cu–Ni (C70600)	[32]	Bal.		0.29	0.008	0.007		1.40				9.44

Table 2

Summary of sites.

Site	Location	Temp. (°C)	pH	DO (ppm ^a) (% sat)	Salinity (ppm ^a)	Sulphate (ppm ^a)	Nitrate (ppm ^a)
PCZ [19,31]							
Immersion (Coco Solo)	Pier 3 km offshore	26.7	8.2	90%	31.4	2430	Trace
Half-tide (Coco Solo)	Pier 3 km offshore	26.7	8.1	87%	31.5	2470	Trace
Marine atmos. (Cristobal)	100 m from coast, 17 m elevation	27			0.015	7.1	1.1
Inland atmos. (Miraflores)	Near Gutan L.	27			0.003	8.8	1.4
Fresh water (Gutan Lake)	Pier 20 m offshore	28.8	7.5	90%	0.013	3240	Trace
90:10 copper–nickel [32]							
Ocean city (New Jersey)	Raft	1–29	7.5–8.2	5.2–11.7	31–34		
Key West (Florida)	Under pier	16–31	8.0–8.2	4–8	33–39		
Port Hueneme (California)	Bulkhead	14–21	7.9–8.1	3.6–5.4	33		
Talara (Peru)	Pier 180 m offshore	18–22	8.2	5–6	35.4		
KeAhole, Kona (Hawaii)	On submerged pipe 45 m offshore	24–28	8–8.3	6–14	34.6–35		
N. Barnard Is. (Australia)	Raft	23–30	8–8.5	5.1–6.5	31.7–37.2		
Sakata harbour (Japan)	Docking pier	2–28	8.4	7.1–13	30.4–32.8		
Genoa harbour (Italy)	Raft	11–25	8.1	4.5–6	35		
Kyndby Isefjord (Denmark)	Raft	0–18	7.5–8.0		18–28		
Studsvik (Baltic) (Sweden)	Bulkhead	2–20	7.4–7.6	6–10	7.8–8.1		
Bohus-Malmon (Sweden)	Raft	2–20	8–8.2	6–10	21–28		
Langstone harbour (UK)	Raft	5–22	7.8–8.4	88–118%	34–34.6		

PCZ: low turbidity, low suspended solids, low biological oxygen demand.

No information for New Haven, Dayton Beach, East Alston.

^a mg/kg.

Copper nickel alloys, widely used in marine applications, have been extensively investigated but for 90:10 there is relatively little information about their longer-term behaviour [24,25]. The most extensive investigation of the cheaper lower nickel content 90:10 copper nickels is the 5 year study conducted at 14 different locations world-wide, in most cases with observations at 0.5, 1, 1.5, 3 and 5 years exposure [32]. Details of the alloys are given in Table 1 and a summary of the exposure conditions in Table 2.

2.2. Copper and high copper bronzes

Corrosion loss data from the 1932 program for high purity (99.97 wt.% electrolytic) copper [26,27] are shown in Fig. 2. It shows the losses as reported for years 8, 10 and 20. It also shows the data for the years 1, 2, 3 and 5 obtained from the readings for total mass including corrosion product (assumed Cu₂O), but converted for the present purposes, using the molecular masses, to obtain (over-) estimates of actual mass losses for these years. The marine exposures were made at Long Island Sound, near Guilford, Conn. and the industrial exposures at Waterbury, Conn. on the roof of a 4 storey factory building adjacent to a (coal burning) steam railroad. The accelerated industrial environment was the same except that the coupons were sprayed with fresh water for 2 min periods four times daily.

The best-fit smooth curves connection the data points in Fig. 2 were obtained using a Stineman [33] function. Also shown are subjective interpretations for the data trend curves, obtained in each case with the trend (closely) anchored to the data points. It is seen that even if the losses for years 1, 2, 3 and 5 are under- rather than

Fig. 2. Corrosion loss data and trends for very high purity (99.97 wt.%) copper drawn from data derived from that reported by Tracey et al. [26] and by Thompson et al. [27]. The losses for years 1, 3 and 5 were reported for coupons without removal of corrosion products. These have been converted to estimated mass losses as would have been obtained after coupon cleaning. The estimates for mass loss (and thus corrosion loss as shown) are likely to be overestimates (see text). Despite this, it is clear that the loss trends are distinctly bi-modal.

over-estimated, the trends in the data are not consistent with the usual power law. Rather they all have bi-modal trends. In addition, the long-term trends are essentially linear, and do not back-project through the origin. Although not shown here, very similar data sets

and trends can be drawn for the other 11 high purity coppers reported [26,27].

Data obtained for commercially high purity copper and various high copper bronzes continuously immersed in the tropical waters of the Panama Canal Zone (PCZ) are shown in Fig. 3. The metric conversions of the corrosion loss data reported by Forgeson et al. [31] and Hummer et al. [19] are shown. As before best fit smooth curves obtained using a Stineman [33] function have been plotted through each data set. There is no subjective interpretation for any of the curves shown.

Each of the trends in Fig. 3 displays a bi-modal trend and each shows the characteristic inflexion (cf. t_a in Fig. 1), after some 3.5 years exposure in the case of 99.9 wt.% pure copper and commercial bronze and after less than 2 years for silicon bronze and at about 2 years for phosphor bronze. Aluminium bronze shows a much longer time to t_a and also much lower overall corrosion losses compared to the others, indicating that it is much more resistant to corrosion than the others.

The corrosion losses for the same set of metals but exposed at half-tide in tidal seawater are shown in Fig. 4. For these data sets bi-modal trends are less obvious than in Fig. 3. The light lines are the best-fit curves obtained using the Stineman smooth curve fitting routine. For pure copper, aluminium bronze and commercial bronze there is a reasonably well-defined change in trend around 6 years of exposure. For silicone bronze a change in trend in the data can be interpreted but for copper and for phosphor bronze rather more interpretation is required. The interpreted trends are shown bold, drawn to over-emphasise slightly the bi-modal behaviour. It is clear in all cases that the power law would not fit any particularly well – the long-term data trends are too long and flat to fit the power law [cf. 19]. As can be seen, the long-term trends (after about 6 years) all are essentially linear. None back-project through the origin.

Data for the same 5 copper alloys exposed to coastal marine atmosphere conditions at Cristobal (PCZ) are shown in Fig. 5. Possibly only the trend for pure copper is consistent with the

Fig. 3. Corrosion loss data and trends derived from mass loss as a function of exposure time for 99.9 wt.% pure copper and various high copper bronzes (Table 1) all subject to continuous seawater immersion exposure in the Panama Canal Zone at Coco Solo. In each case the trends are bi-modal, without any interpretation being required. Data from [19,31].

Fig. 4. Corrosion loss data and trends derived from mass loss as a function of exposure time for 99.9% pure copper and various high copper bronzes (Table 1) all subject to continuous seawater exposure at half-tide in the Panama Canal Zone at Coco Solo. All the trends are inconsistent with the power law and can be interpreted as showing an early bi-modal characteristic (i.e. in the range 0–4 years). Data from [19,31].

power law but this is not the case for the others. As before best fit trends and interpreted trends are shown. Again, the long-term trends are closely linear and do not back-project through the origin.

The data set for each of the same 5 alloys exposed to inland atmospheric conditions some 1.5 km inland from Miraflores (PCZ) (Fig. 6) shows a considerable departure from a simple power law relationship and is much clearer showing a bi-modal trend. They all appear to have an inflexion at around 3 years exposure. This is evident in the best-fit (light) trend lines and also in the bold but subjective trend lines. In these cases also, the data for the long-term exposures trend (almost) linearly, and do not back-project through the origin.

The above cases all involved seawater or seawater spray derived from Panama Canal seawaters (Table 2). In contrast, very low chloride content was present in the nominally fresh waters of Gutan Lake (PCZ) (Table 2). Fig. 7 shows the corrosion loss trends for the same set of copper alloys as before. No interpretation is required to see that each data trend is bi-modal, although this is less clear for 99.9 wt.% pure copper. Bold trend lines have been drawn to emphasise how the data can be interpreted as bi-modal.

In this case the development of the second mode of the bi-modal characteristic takes much longer to develop than in the previous environments. Perhaps for this reason any linearity of the long-term trend is not obvious within the 16 year exposure period.

2.3. Copper nickel alloys

Two selections of corrosion loss and pit depth data from the five-year program [32] for 90:10 copper nickel (Table 1) immersed at temperate and tropical sites are shown in Figs. 8 and 9. Not all data is presented as some of the sites were determined, subsequently, to have been subject to high levels of water pollution. Details of the sites considered herein are shown in Table 2. In Fig. 8, two of the data trends are clearly bi-modal and for the other two only a limited amount of subjective interpretation is required to reveal the bi-modal trend. Again, the long-term parts of the trends are closely linear.

Three sets of corrosion loss data for 90:10 copper nickel alloy immersion exposed to the colder coastal seawaters of the North Atlantic are shown in Fig. 9, again with, in light lines, best fit trends

Fig. 5. Corrosion loss data and trends derived from mass loss as a function of exposure time for 99.9 wt.% pure copper and various high copper bronzes (Table 1) all subject to marine atmospheric exposure in the Panama Canal Zone at Cristobal. All the trends are inconsistent with the power law and can be interpreted as showing an early bi-modal characteristic (i.e. in the range 0–4 years). Data from [19,31].

Fig. 6. Corrosion loss data and trends derived from mass loss as a function of exposure time for 99.9% pure copper and various high copper bronzes (Table 1) all subject to inland atmospheric exposure in the Panama Canal Zone at Miraflores. All the trends are inconsistent with the power law and can be interpreted as showing an early bi-modal characteristic (i.e. in the range 0–4 years). Data from [19,31].

Fig. 7. Corrosion loss data and trends derived from mass loss as a function of exposure time for 99.9 wt.% pure copper and various high copper bronzes (*Table 1*) all subject to continuous fresh water immersion exposure in Gutan Lake (PCZ). Apart from pure copper, the trends are inconsistent with the power law and can be interpreted as showing a bi-modal characteristic. Data from [19,31].

Fig. 8. Corrosion loss as a function of exposure time for 90:10 copper nickel alloy plates subject to continuous temperate seawater immersion exposure at various sites, together with interpreted bi-modal trends. Data from [32].

Fig. 9. Corrosion loss as a function of exposure time for 90:10 copper nickel alloy plates subject to continuous cool seawater immersion exposure at various sites together with interpreted bi-modal trends. Data from [32].

Fig. 10. Corrosion loss as a function of exposure time for 70:30 copper nickel alloy subject to continuous seawater immersion exposure at Coco Solo (PCZ) together with best fit and interpreted (bold) trend lines showing clear bi-modal trend. Data from [19,31].

and, in bold, the corresponding interpreted trends. Although corrosion is much slower in colder waters, even in these cases the data clearly shows trends that are bi-modal in character, even though not as fully developed as in earlier examples in warmer conditions. For 70:30 copper nickel *Fig. 10* shows long-term data obtained at Coco Solo (PCZ). Again, the trend corrosion loss trend is bi-modal.

2.4. Copper zinc alloys

Figs. 11 and 12 show data reported by Brock [5] for copper C11000 and copper alloys C26000 and C70600 exposed to atmospheric corrosion at 3 different US mainland sites. These are New Haven (CT), considered representative of an industrial atmosphere, East Alton (IL) representative of a severe industrial atmosphere, and Dayton Beach (FL) representative of a marine environment with negligible pollution. The data trends in *Fig. 11* are obviously bi-modal even without interpretation. Those in *Fig. 12* can be

Fig. 11. Corrosion loss data for copper alloy C26000 (70:30 Cu:Zn) for 3 atmospheric corrosion sites. Light trends are best-fit trends and bold lines are subjectively interpreted trends. Data from [5].

Fig. 12. Corrosion loss data for commercially pure copper (C11000), 70:30 Cu:Zn alloy (C26000) and for 90:10 copper nickel alloy (C70600) exposed for up to 20 years at the industrial exposure site at New Haven (CT). Light trends are best-fit trends and bold lines are subjectively interpreted trends. Data from [5].

interpreted easily as bi-modal. None are obviously consistent with the power law.

3. Maximum pit depth data and trends

Very little data has been reported in the literature for the pitting of copper and copper alloys, either as a function of exposure period or as multiple readings that can be used for pit depth uncertainty (variability) estimation. Observations for copper-nickel (90:10) at a range of exposure sites (Table 2) [32] provide some insight. The development of pit depth with increased exposure time for a range of water temperatures is shown in Figs. 13–15. These show that all trends for pit depth are bi-modal, with only little data interpretation required. For a number of other sites in this test program the data for maximum pit depth are erratic, showing very deep pit depths with much lower subsequent pit depths. Such trends are counter to expectation as represented by the power law model

Fig. 13. Maximum pit depths for 90:10 copper nickel (C70600) immersed in seawater at 3 different sites in Scandinavia for which the seawaters were considered to be unpolluted. Some interpretation is required to extract the bi-modal trends shown with, as in the case of the less than fully aerated Studsvik site, the long-term data ignored. Data from [32].

Fig. 14. Maximum pit depths for 90:10 copper nickel (C70600) immersed in seawater at 3 different temperate seawater sites. Apart from the data for Sakata harbour, little interpretation is required. Data from [32].

or by the possibility of a bi-modal trend. Here it is observed that in the notes accompanying the data it is noted that the very deep pits are actually crevice corrosion, observed as occurring under the holders of the coupons. Examination of data for depth of pit or crevice corrosion suggests that these are erratic with respect to exposure period for those cases where the sites were likely to have been subject to considerable water pollution [32]. This matter is discussed further below.

Observations for maximum pit depth and also the average of the 20 deepest pits for commercially pure copper and for two copper alloys reported from investigations in the Panama Canal Zone [31] are shown in Fig. 16. In this case all three data sets show measured pit depths at 2 years of exposure that are greater than the pit depths measured subsequently. The notes accompanying the data in the original source document [31] record the reported pitting in each case being associated with 'local attack' or 'random fouling'. Such behaviour was not observed for any of the other copper alloys in the same test program and exposed to the same environment throughout. These other copper alloys all showed either very

Fig. 15. Corrosion pit depth data and trends for 2 different sites. The trend for Genoa harbour shows a higher than expected second mode (i.e. deeper pits for longer exposure times). Data from [32].

shallow or zero pit depths throughout the total 16 year exposure period. There is no mention of the type, extent or severity of biofouling.

4. Discussion

In considering why the bi-modal characteristic appears so often in the data sets considered above, it is necessary to consider the development of the corrosion process as the corrosion products build-up on the metal surface. As noted, for commercially pure copper in the (wet) atmosphere, Tammann [4] proposed that the build-up of corrosion products renders inward diffusion of oxygen increasingly more difficult and that this gradually polarises the cathodic reaction. Mathematical formulation of this concept led to the widely-applied power law $c(t) = At^B$ where $c(t)$ is corrosion loss, t is time and A and B are constants obtained from fitting the function to data. Its derivation has been refined [34,35] but the overall form remains the same after simplifications. Since it is meant to represent the reduction in corrosion as a direct result of reduction in oxygen diffusion, it may be taken as applicable to phases 0–2 of the bi-modal model in Fig. 1, that is prior to t_a when oxygen diffusion is corrosion rate-controlling (except perhaps in the very early stages, such as phase 0 [20–22]). After t_a the corrosion process changes to being under wholly or partly anoxic corrosion conditions. For the corrosion of steels the change from phase 2 to phase 3 has been associated [36] with high degrees of pitting corrosion and with autocatalytic corrosion, following the model proposed originally by Wranglen [37]. In that model the dissociation of water provides the required electron acceptor (H^+), lowering the pit pH and also results in the evolution of hydrogen gas. A similar mechanism has been used to provide a rationale for the bi-modal trend of aluminium alloys [22]. However, the direct application of this mechanism to copper is problematic since corrosion of pure copper under anoxic wet environments usually is considered thermodynamically impossible [3]. Although there have been reports of experimental observations to the contrary [38,39] others have been unable to verify them, leading to the proposition that they were the result of extremely small impurities in the test solutions [40]. In any case, all the experiments show either zero or negligible corrosion.

Under aerated conditions pitting of copper surfaces usually is very mild. However, severe pitting (and crevice corrosion) has been observed, mainly under surface deposits and detritus, and under

Fig. 16. Estimated absolute maximum pit depths and the average of the 20 deepest pits as functions of the period of immersion exposure period at Coco Solo (PCZ) for 3 different copper alloys. Data from [19]. The trends shown are best-fit trends.

marine organisms [8], and also under carbon or calcium carbonate deposits [41]. In addition, pitting for copper has been associated with de-aerated and low pH conditions inside pits or crevices [8]. In consequence, it may be postulated that earlier corrosion products produced by copper corrosion can provide the conditions necessary for subsequent pitting (or crevice corrosion). This is similar to the conditions necessary for pitting corrosion according to Wranglen's model [37] but, as noted, the limitations imposed by the thermodynamics of the hydrogen ion reduction reaction do not permit the direct application of that model to copper. Another mechanism must provide the necessary aggressive conditions inside pits.

The mechanics of pitting corrosion of copper have not been discussed extensively in the literature. Lucey [42,43], building in part on the observations by May [41] and Campbell [44], proposed that the rapid rate of metal dissolution in the pits is the result of the reduction of cupric ions to cuprous ions under de-aerated conditions. This was assumed driven by the relative concentration of cuprous ions on the two sides of the thin membrane of cuprous oxide (Cu_2O) that forms the pit cover. In turn this was assumed to depend, in part, on the semi-conductive properties of Cu_2O [45]. Interestingly, the model did not rely on the small anode–large cathode concept usual for pitting. In common with other pit models, it does, however require a sufficient supply of reducible ions, such as chloride or sulphate ions, into the pit to maintain charge equilibrium. In turn this is assumed to be responsible for the rapid rate of metal dissolution. The mechanism responsible for the subsequent reduction of the corrosion rate has been proposed as the build-up of Cu_2O on the inside of the membrane reducing both its ionic and its electronic resistance [42].

Assume now that the above represents a simplified but not implausible description of the transient development of pitting for copper under de-aerated conditions. It can be taken, therefore, as a description of the conditions at the end of phase 2 (Fig. 1) when localised de-aerated conditions are considered to have established, similar to the conditions under surface deposits, detritus, etc. and for which aggressive crevice and pitting corrosion of copper has been observed [8]. These conditions also will apply at the start of phase 3 of the bi-modal model. The way is now open for development of a simple mathematical model for the description of corrosion in phase 3.

As in the original Tammann [4] model, assume that the corrosion can be idealised as an equivalent general corrosion and that

the instantaneous rate of that corrosion $dc(t)/dt$ is proportional to the diffusivity $D(t)$ at that time t :

$$\frac{dc(t)}{dt} = k_1 D(t) \quad (1)$$

where k_1 is a constant. Also, assume that diffusivity reduces with increasing corrosion $c(t)$ and that this depends directly on the instantaneous diffusivity $D(t)$ at that time:

$$\frac{dD(t)}{dc(t)} = -k_2 D(t) \quad (2)$$

where k_2 is a constant and with the sign denoting that diffusivity $D(t)$ reduces as corrosion $c(t)$ increases. Re-arranging and integrating produces:

$$D(t) = \exp[-k_3 c(t) + k_4] = k_5 \exp[-k_4 c(t)] \quad (3)$$

This shows that the diffusivity is a function of time (t) and that it depends on the corrosion loss that has occurred to that point in time. Substituting in Eq. (1) produces:

$$\frac{dc(t)}{dt} = k_1 k_5 \exp(-k_4 c(t)) \quad (4)$$

from which it follows, after integration and re-arrangement that:

$$c(t) = k_7 \ln(k_6 t + 1) \quad (5)$$

Using the initial conditions $c(t) = c_a$ at $t = t_a$ and using new constants M_i $i = 1, 3$ produces:

$$c(t) = M_1 [1 + M_2 \ln(t + M_3)] \quad (6)$$

Expression (6) is similar to the 'logarithmic law' proposed previously by Evans [34] but for corrosion starting from zero initial conditions – in this case Eq. (6) reduces to $c(t) = M_2 \ln(t + M_3)$. His derivation was based on the notion of so-called 'mutually blocking pores' in the rust layers in the very early stages of exposure of newly corroding metals under oxygen diffusion conditions. This can be interpreted as similar to the approach used herein for the diffusion of species through the Cu_2O membrane covering individual pits, with diffusion through the membrane reducing as the membrane grows in thickness and some or all of the pores of the original membrane becoming constricted or blocked. It follows that the parameter M_1 in Eq. (6) can be interpreted as the fraction of the total surface area occupied by the membranes covering individual pits.

The above was derived to represent phase 3 of the model (Fig. 1). For longer-term behaviour it may be assumed that diffusion limitations also extend into phase 4, although the species in the rate controlling process almost certainly will be different. Most likely the outward diffusion of copper corrosion products becomes rate-limiting. However, this cannot be confirmed as no detailed reports of long-term mechanisms in copper corrosion appear to be available. The corrosion outcomes, however, suggest a steady-state mechanism, consistent with the repeated appearance of an apparently linear long-term trend, as seen in many data sets (Fig. 4–8). These linear trends do not back-project through the origin and are inconsistent with the power law, since it has no asymptotic characteristic.

With this background it is possible to reconsider the data trend shown in Fig. 7(a) for 99.9% pure copper in nominally fresh (but slightly chlorinated) water (see Table 2). To consider this case in more detail, the data has been re-plotted in Fig. 17. Also shown is the classical power law $c(t) = At^b$ fitted to the entire data set. Evidently it is not a particularly good fit. The question arises whether the data can be better represented by a bi-modal trend. To consider this, assume that for phases 0–2 the power law is valid, consistent with its original derivation for the oxidation of copper [4] although as. 1 suggests, it is unlikely that a single function

Fig. 17. Data from Fig. 7(a) for pure copper in (slightly chlorinated) fresh water. Also shown is the classical power law (solid line) and two functions (broken lines) (see text) to represent the bimodal model, with the change-over between modes taken as 2 years. Clearly the latter is a better fit to the data.

can represent each of the 3 phases involved. Nevertheless when plotted in Fig. 17 for the first 2 years it appears an acceptable approximation.

To represent the trend for the subsequent years, Eq. (6) is fitted to that data (Fig. 17). It is seen to be a reasonably good fit. Obviously, for each of these two curves fewer data points are involved, making fitting easier and producing fitting correlation coefficients very close to unity. The important point is that the two expressions produce distinctly different curves that show a change in corrosion rate from the end of phase 2 to the beginning of phase 3. Although not shown, the result does not change very much if a different change over point (e.g. 4 years) is used. This supports the notion that the underlying trend in the data is bi-modal, even though for this example it was not strongly in evidence in Fig. 7(a). The same approach was tried for other examples. In all cases fitting the power law to the early data (phases 0–2) and Eq. (6) to the later data (phases 3–4) provides a more consistent representation of the data.

Over-viewing the trends for commercially pure copper in the various exposure environments shows that for relatively aggressive environments, such as for marine immersion (Figs. 3 and 4) or tidal exposures or industrial atmospheres (Fig. 2) the bi-modal characteristic is very clear. Conversely, for very low saline environments (Fig. 7) and for the unpolluted atmospheric environments (Figs. 5 and 6) the trends in the data are not strongly bi-modal. Although it cannot be verified using the present data, this does suggest that the bi-modal characteristic would be even less pronounced for ultra-pure copper and for pure water conditions. If so, it would be consistent with the assumptions made for pure copper and presumed clean groundwater environments in studies for nuclear waste containment [3].

Similarly, over-viewing the trends for the various copper alloys considered herein and their exposure environments, suggests that the bi-modal characteristic generally increases with alloy content. As for pure copper, it also appears to be greater for saline and polluted industrial exposure conditions as compared with those under only partly or sporadically saline or low levels of atmospheric pollution. Taken together, this indicates that alloy composition and the environment are the two major influences for the degree of bi-modal characterisation for copper alloys. The extent to which these possible influences can be verified with data and the possible functional relationships involved remains for further research.

Fig. 18. A set of coupons all from the same batch of 90:10 copper nickel after 5 years continuous immersion exposure at North Barnard Island, Pacific Ocean, Australia. The site is tropical and considered unpolluted [32]. The right coupon shows 9 points of localised biofouling rather than general biofouling as for the others (photograph courtesy of DSTO, Melbourne).

Turning now to the data and trends for maximum pit depth, it is noted that in the majority of cases for which data is available the bi-modal trend is clearly evident. However, the apparently anomalous observation of very high early pit depths followed by lower subsequent pitting depths requires consideration.

One possible reason is that each of the observations was obtained from separate coupons. It is known that in natural exposure environments, settlement of biofouling and hence localised corrosion may be different for different surfaces (i.e. coupons) and this has been noted also for copper and copper alloys [8]. An example is shown in *Fig. 18* for a set of 90:10 copper nickel coupons after five years of exposure in the Pacific Ocean at North Barnard Island, Australia. The site is considered unpolluted [32]. The six coupons were all from the same source and, with one exception, show almost identical exterior corroded surfaces with biofouling evident. The right coupon shows little evidence of general biofouling but instead has several (about 9) highly localised points of what appears to be concentrated biofouling. Other, earlier field observations indicate that these are likely to be points of intense pitting [8]. If this is correct they would require a large cathodic area and tend to eliminate or much reduce corrosion elsewhere. That indeed appears to be the case as judged from visual appearance.

However, this does not explain the consistency between the three alloys shown in *Fig. 16*. Each data set has the maximum pit depths only for those coupons recovered at year 2, but not at any subsequent time. The occurrence of three such results suggests that they are unlikely to be the result of chance, of processing or of reporting errors. This proposition is reinforced by the erratic trends for maximum pit depth for the sites in the 90:10 copper–nickel study [32] that are known from other analyses [46] to have been polluted at the time the exposure program was carried out. Copper nickels are known to be prone to microbiological influenced corrosion and related severe pitting under pollution conditions [8].

Another explanation is considered more likely. For the 90:10 copper nickel study the notes accompanying the data state that the deepest corrosion was observed to be crevice corrosion under the coupon holders [32]. This is also the case for the data used to draw the trends shown in *Fig. 16*. They are accompanied by notes stating that the deep pitting observed at 2 years exposure was very localised and that biofouling was likely [31]. It is well-known that highly localised, aggressive corrosion can occur under deposits and other conditions that facilitate differential aeration, and that this applies also for copper alloys [8]. However, an important question is why the maximum pit depth subsequently appears to reduce with increased exposure period (*Fig. 16*).

A possible explanation lies in so-called ‘reverse crevice corrosion’. It refers to the phenomenon of pits or crevices in copper

gradually becoming clogged with corrosion product as a result of limited outward diffusion of species from pits or crevices relative to the rate of inward diffusion of other species [47]. This means that subsequent measurements of pit depth could be to the corrosion products rather than to the remaining metal, thereby measuring less deep pits. Also, new pits or crevices have been observed to initiate on the periphery of pit or crevices that have become clogged. The usual explanation is that this is the result of new, localised, differential aeration cells forming around the previous crevice or pit mouth [6,48], although other authors claim the mechanism is still not understood [49]. In principle the process could recycle with time. The net result would be that the maximum depth of pitting appears to be reducing in depth at first and then steadying with increased exposure time. This is what *Fig. 16* appears to show.

One further factor sometimes raised is that results such as those described above were obtained from field experiments that used observations of pit depth from different coupons at each observation time point. With the current state of the art the measurement of the development with time of corrosion pit depth for one particular pit is precluded. Different coupons must be used for different exposure periods. This adds an additional degree of uncertainty and thus variability. However, it is unlikely to be responsible, solely, for the apparently anomalous observation of decreasing maximum pit depth with increased exposure time. It is considered that the trends shown in *Fig. 16* are too stark and too repetitive to be the result only of variability. Possibilities for influences that may be involved remain as a matter requiring further detailed investigation to be fully resolved.

Finally, the strongest support for the applicability of the bi-modal trend for copper and copper alloys lies in its pervasiveness. It is clearly evident in some data sets without requiring re-interpretation. In other cases a bi-modal trend can be constructed easily through the available data points, although alternatives cannot be ruled out. The reason for this is the amount of data available is not always quite sufficient, since most often exposure programs and coupon recoveries were determined on an experimental plan based on the power law being assumed the correct description for corrosion progression. As a result, most field programs have used a logarithmic spacing of observation points in time. Nevertheless, it is clear from the data trends that there is a high degree of consistency in the observation of the bi-modal trend across different alloys, and across different exposure conditions and exposure sites. In particular, there is a high degree of internal consistency between data sets, for example between exposures in fully immersed conditions, in tidal conditions, for splash and for marine atmospheric exposures. Usually these show a gradual change in the data sets consistent with what would be expected, but the bi-modal trend largely remains.

5. Conclusion

The following conclusion may be drawn:

1. The data for copper and high copper alloys, including 90:10 and 70:30 copper–nickel, previously published in the open literature may be interpreted as in most cases showing a bi-modal function for corrosion loss and for maximum pit depth development with increased exposure time. This was found for immersion, mid-tide, coastal and inland marine exposures, for fresh water immersion exposures and for inland and industrial atmospheric exposure conditions.
2. For high purity copper the early part of the second mode of the bi-modal characteristic most likely involves autocatalytic pitting under deposits of earlier copper corrosion products. The data considered herein indicates that the intensity of the second mode has a strong dependence on the chloride concentration in the exposure environment.
3. For copper alloys the available data indicate that the alloying elements also may be involved in contributing to the second mode. However, the mechanisms involved remain to be investigated.
4. In most cases the eventual long-term trend for corrosion is a linear function of time that does not back-project through the origin. This is consistent with the bi-modal model but not with the power law since it does not possess a linearly asymptotic property.
5. Maximum pit depths for copper and copper alloys sometimes show trends with high early pit depths and decreasing pit depths for longer exposures. This was found for different copper alloys and across different exposure programs. It is proposed that it is the result of the same phenomenon sometimes described as 'reverse crevice corrosion' in which the deeper pits are filled with corrosion products and subsequent pit depth measurements are for other, less developed and therefore less deep pits or crevices. It also remains a matter for further investigation.

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