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Effect of sulfide on the stress corrosion behaviour of a copper-aluminium alloy in saline water

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The stress corrosion cracking (scc) behaviour of α-Al bronze was investigated in 3.4% NaCl with sodium sulfide contaminations under open-circuit potentials, as well as at different applied potentials using the constant slow strain rate technique. The susceptibility of α-Al bronze towards stress corrosion cracking has been found to increase with an increase in sulfide ion concentration and in anodic potentials. The increase in sulfide ions in polluted saline water resulted in a reduction in the maximum stress (σ max). The results support film rupture and anodic dissolution at slip steps as the operating mechanism of the stress corrosion cracking process.

1. Introduction

Copper-base alloys have an attractive combination of properties e.g. good machinability, high thermal and electrical conductivity and resistance to biofouling [1, 2]. Aluminium bronzes (Cu-Al) are an important class of copper base alloys, which have good strength and corrosion resistance [3, 4]. Small quantities of Fe, Ni, Ag may be added to Al-bronzes to modify their mechanical properties or corrosion resistance [3–7]. These Al-bronzes have been used in various sea water applications [1, 4, 8, 9]. Their corrosion resistance was attributed to the formation of a film of Al_2O_3, which heals rapidly when damaged [10].

Stress corrosion cracking (scc) failures in Al-bronzes have been reported, for instance, in Mattsson's solution [11], in marine and desalination environments [12], in 3.4% NaCl solution [13] and in sodium nitrite solution [14]. Various pollutants are often introduced in seawater by decomposition of seaweed [15]. Sulfide pollution of seawater can occur in many ways, such as from rotting vegetation, and from industrial waste discharge. Anaerobic sulfate-reducing bacteria can produce sulfide but only under oxygen-free conditions [16]. Recent investigations [17–22] were conducted on the corrosion of copper-nickel alloys in sulfide polluted seawater. Electrochemical polarization measurements and slow strain rate tests have been reported [23] on the susceptibility of 90 Cu-10 Ni alloy to stress corrosion cracking in sea water polluted by sulfide ions.

The objective of this paper is to study the susceptibility of α-Al bronze to stress corrosion behaviour in 3.4% NaCl with sulfide contamination under various conditions.

2. Experimental procedure

The material used was α-Al bronze which was supplied by the Non-Ferrous Industries Company, Helwan, Egypt, with the composition: 7% Al, 0.04% iron (Fe), 0.01% nickel (Ni), 0.04% silicon (Si), 0.006% magnesium (Mg), and the balance Cu. The mechanical properties are: Ultimate tensile stress (UTS) was 150 kg/mm^2, Brinell hardness (HB) number was 100 kg/mm^2, and elongation was 6%. A constant slow strain rate machine was used at a constant strain rate of 0.9×10^{-6} s^{-1}. The specimens were machined to a gauge length of 35 mm and a diameter of 6 mm. They were polished with 320-, 600-, and 800-grit silicon carbide (SiC) paper, degreased with acetone, and coated with paraffin wax so that only the gauge length was exposed to the solution. The experiments were carried out at $24 \pm 1°$C in air, and in aerated 3.4% NaCl with different concentrations of sodium sulfide (5, 10, 20 ppm). The potential was controlled using a potentiostat. Potentiostatic polarization experiments were carried out on unstressed specimens. The potentials were measured using a saturated calomel reference electrode and reported relative to the normal hydrogen electrode (NHE). Potentiostatic polarization curves were measured using potential steps of 20 mV min^{-1}. The potential was controlled using a Wenking Potentiostat L.T.73.

The cell used was a 200 ml glass cylinder, closed by upper and lower stoppers, through which the ends of the specimen protruded. A platinum sheet was used as a counter electrode. Cracked specimens were removed from the solution after failure, cut 1 cm beyond the crack tip, and subjected to scanning electron microscopy (SEM) using a JEOL, JSM-T20 (Japan).

3. Results and discussion

3.1. Stress-time measurements

Stress-time curves were measured in 3.4% NaCl in the presence and absence of different concentrations of sodium sulfide under both open circuit conditions and controlled potentials. Measurements were also performed in air for comparison. The results are shown in Figs 1 and 2 and summarized in Table I. The stress

TABLE I Stress corrosion cracking parameters of α-Al bronze in 3.4% NaCl solution with sodium sulfide contaminations

Medium	Potential mV_{NHE}	Time to failure h	Time to failure min	r^a	τ^b	S^c	Mode of failure
Air	—	3	10	1.00	1.00	0.00	ductile
3.4% NaCl	OCP	2	45	0.93	0.86	0.10	ductile
3.4% NaCl + 5 ppm S^{2-}	OCP	2	48	0.96	0.88	0.07	ductile
3.4% NaCl + 10 ppm S^{2-}	OCP	2	54	0.95	0.92	0.06	ductile
3.4% NaCl + 20 ppm S^{2-}	OCP	2	53	0.87	0.91	0.11	Brittle (microcracks)
3.4% NaCl + 20 ppm S^{2-}	200	3	—	0.92	0.94	0.07	brittle
3.4% NaCl + 20 ppm S^{2-}	400	2	40	0.88	0.84	0.14	brittle
3.4% NaCl + 20 ppm S^{2-}	−20	2	39	0.95	0.84	0.09	ductile
3.4% NaCl + 20 ppm S^{2-}	−200	2	33	0.95	0.81	0.10	ductile

[a] $r = \sigma_{max}(\text{sol.})/\sigma_{max}(\text{air})$.

[b] $\tau = t_f(\text{sol.})/t_f(\text{air})$.

[c] S = susceptibility to scc.

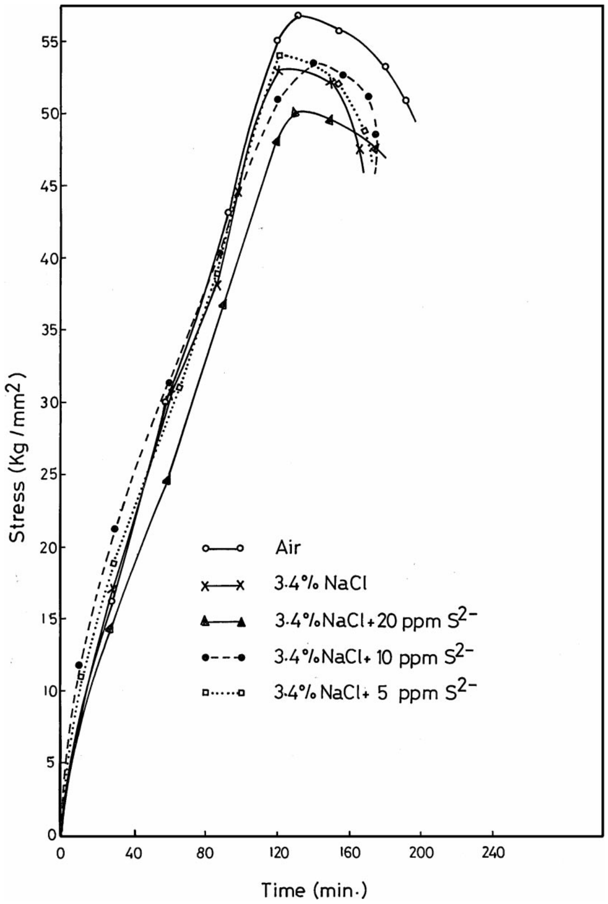


Figure 1 Stress-time curves of α-Al bronze in 3.4% NaCl in the presence and absence of different concentrations of sodium sulfide at open-circuit potential (OCP).

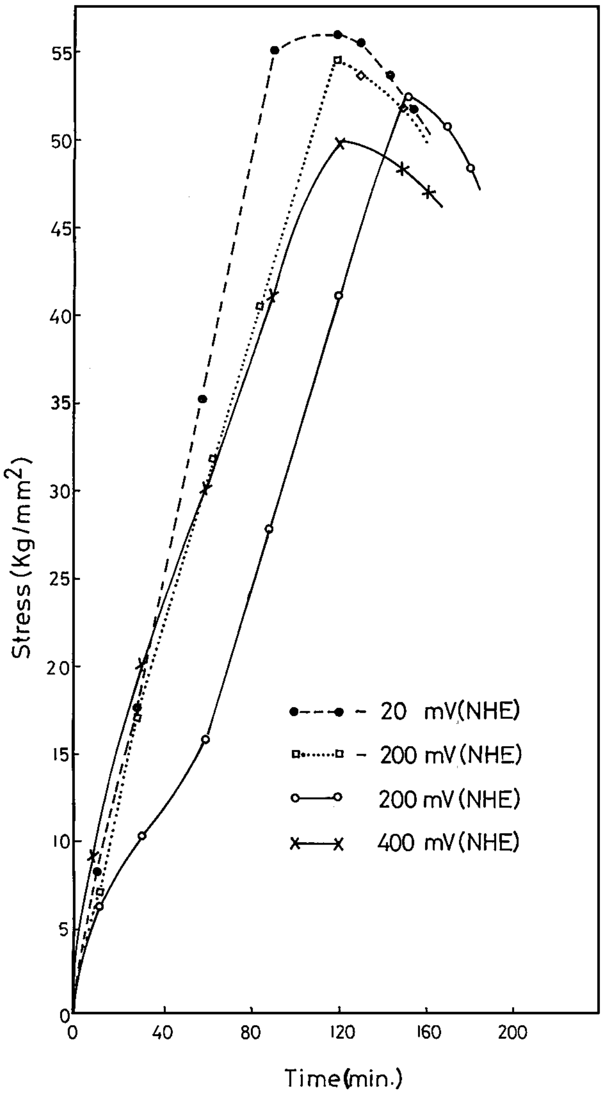


Figure 2 The effect of potential on the stress-time curves of α-Al bronze in 3.4% NaCl + 20 ppm Na_2S.

increased with time up to the maximum yield stress (σ max) before it declined until failure at t_f. The susceptibility to stress corrosion was measured by the ratios of both the time to failure (τ) and the maximum stress (r).

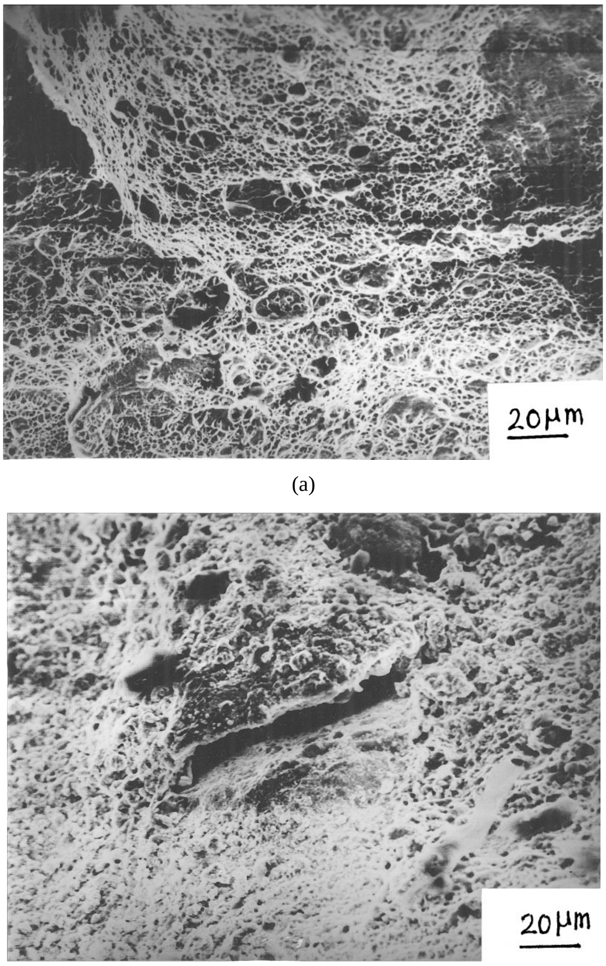
The maximum stress ratio is defined as

$$r = \frac{\sigma_{max}(\text{sol.})}{\sigma_{max}(\text{air})} \tag{1}$$

and the ratio of time to failure

$$\tau = \frac{t_f(\text{sol.})}{t_f(\text{air})} \tag{2}$$

The values of r and τ and the metallographic appearance of the fracture surface are useful criteria for assessing susceptibility to stress corrosion cracking (scc). In



(a)

(b)

Figure 3 SEM fractographs of α-Al bronze in (a) air and (b) 3.4% NaCl + 10 ppm Na_2S, at OCP.

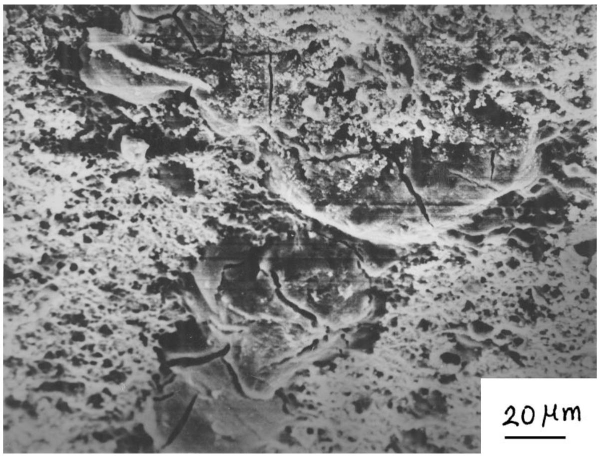
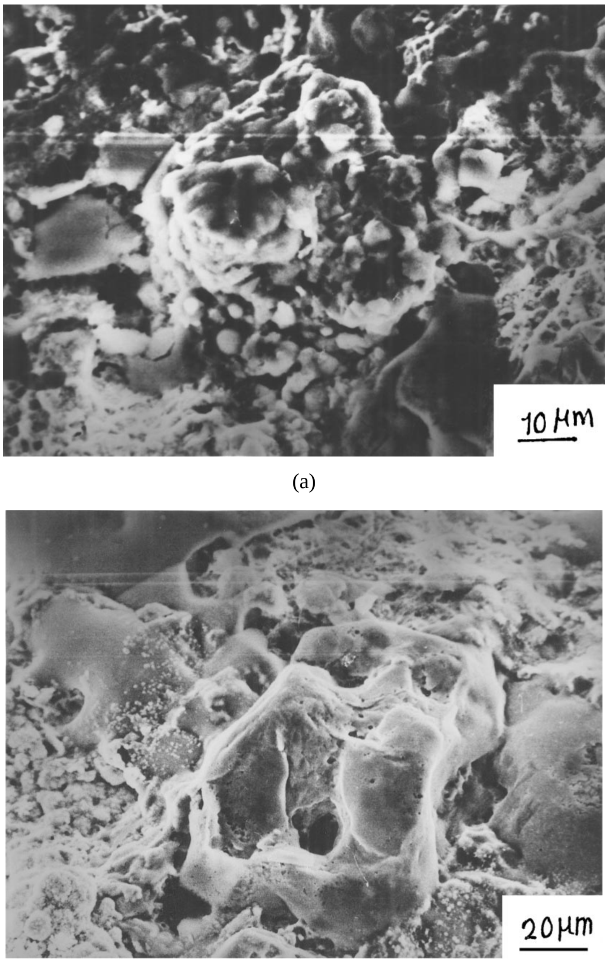


Figure 4 SEM fractographs of α-Al bronze in 3.4% NaCl + 20 ppm Na_2S at OCP.



(a)

(b)

Figure 5 SEM fractographs of α-Al bronze in 3.4% NaCl + 20 ppm Na_2S at (a) 200 mV_{NHE} (b) 400 mV_{NHE}.

previous work [24] both r and τ were combined in a quantitative phenomenological expression for the susceptibility (s) to scc, given by:

$$S = [(1 - r)(1 - \tau)]^{1/2} \qquad (3)$$

Fig. 1 illustrates the stress-time curves obtained in 3.4% NaCl in the presence and absence of different concentrations of Na_2S under open-circuit potential (OCP). The increase of sulfide ion concentration led to a reduction in the maximum stress. The effect of potential on the stress-time curves in 3.4% NaCl + 20 ppm S^{2-} is shown in Fig. 2. It reveals that an increase of the anodic potential reduces the maximum stress endured by α-Al bronze before failure. The metallographic appearance of the fracture surfaces in most tests under OCP and cathodic potentials displayed ductile failure (see e.g. Fig. 3). Some microcracks are evident on the brittle fracture surface in Fig. 4. These microcracks are believed to have been caused by the increasing aggressivity of sulfide polluted saline water (20 ppm). Fig. 5 shows a brittle failure for the alloy in 3.4% NaCl + 20 ppm S^{2-} under anodic potentials. Table I summarizes the above results. The effects of potential on r, τ and s are shown in Fig. 6. It reveals that r, τ and s are affected only slightly by changes in potential. The above evidence indicates that scc of α-Al bronze in 3.4% NaCl + 20 ppm S^{2-} occurred mildly at the higher potentials ($\geq$200 mV_{NHE}). These observations find interpretation in the following: (i) the effects of both chloride and sulfide ions depend on the electrode potential (which is a measure of the oxidizing power of the electrolyte in absence of potential control), (ii) the severity of cracking increases with the increase of applied external anodic polarization and (iii) under the potentials range mentioned above, the sulfide ion results in an increase in the measured anodic current. The increase of current may be attributed to the anodic oxidation of the

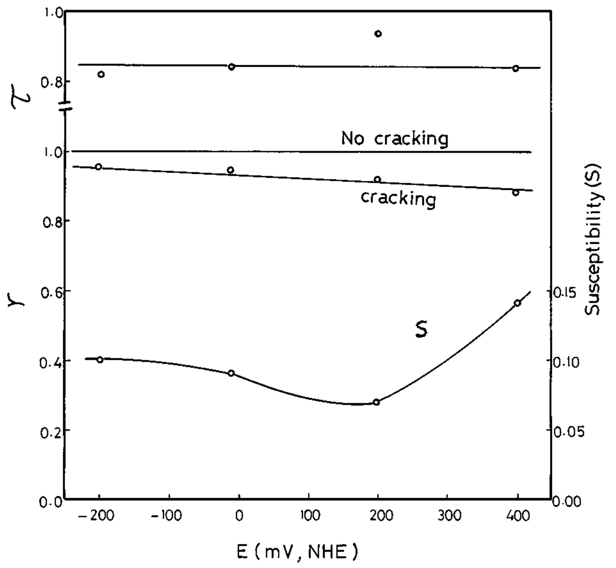


Figure 6 Effect of potential on r, τ and s for α-Al bronze in 3.4% NaCl + 20 ppm Na_2S, see text.

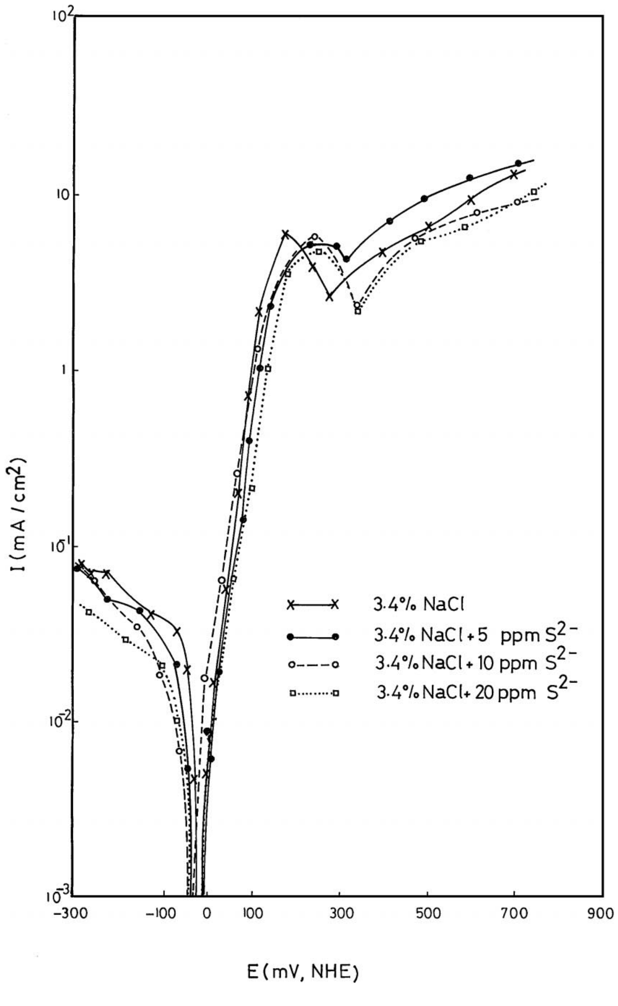


Figure 7 Potentiostatic polarization curves of α-Al bronze in 3.4% NaCl in the presence of different concentrations of sodium sulfide.

sulfide ion. The propensity of α-Al bronze to scc depends on the sulfide ion concentration in the seawater which increases the severity attack.

3.2. Electrochemical measurements

Fig. 7. Illustrates the polarization curves of α-Al bronze in 3.4% NaCl in the presence of 5, 10 and 20 ppm sulfide ions. The current increases abruptly with potential at values near the OCP. At cathodic potentials to E_{corr}, the current is a measure of by the oxygen reduction reaction (cathodic reaction in aerated seawater)

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-. \qquad (4)$$

However, generally, the pollution of seawater with sulfide results in corrosion problems with Cu-base alloys due to the formation of Cu_2S. The formation of black cuprous sulfide (unstable) occurs via:

$$2Cu + S^{2-} \rightarrow Cu_2S + 2e^- \qquad (5)$$

According to Tromans *et al.* [25] Cu is also involved in this reaction:

$$2Cu + H_2O \rightarrow Cu_2O + 2H^+ + 2e^- \qquad (6)$$

Recently, Ateya *et al.* [9, 13] as well as Schussler and Exner [26] identified Al_2O_3 as an inner adherent layer, acting as a barrier for ionic transport across the corrosion product.

$$2Al + 3H_2O \rightarrow Al_2O_3 + 6H^+ + 6e^- \qquad (7)$$

Another outer layer of Cu_2O was also identified, both were detected by X-ray diffraction and Auger electron spectroscopy (AES) techniques on Al-bronze surfaces in sodium chloride solutions. Pickering *et al.* [17] suggested that the higher corrosion rates of Cu-9.4 Ni-1.7 Fe in sulfide contaminated 3.4% NaCl solution are due to a highly defective Cu_2O layer containing Cu_2S which permits rapid ionic and electronic transport through it. The Cu_2S is less protective than Cu_2O. The experimental work reported here is directed specifically at evaluating the susceptibility of α-Al bronze to scc in 3.4% NaCl containing sulfides in the range of 5 to 20 ppm. It is clear that the corrosion current decreases slightly as the sulfide concentration increases as shown in Fig. 7. This is in agreement with the results have been reported by El-Domiaty *et al.* [23].

Fig. 8 illustrates the effect of potential on the current-time curves of α-Al bronze in 3.4% NaCl + 20 ppm S^{2-} with (w) and without (w/o) stress condition (i.e. applied a constant strain rate). The α-Al bronze system shows an increase of current density values under anodic potentials as compared to cathodic potentials with and without stress. This result confirmed that the scc of α-Al bronze observed under high anodic potentials was caused by anodic dissolution. The anodic dissolution current supported by the surface of the bare alloy increases under the effect of the applied stress as a result of the breakdown of the oxide film which is known, due to the formation of a slip steps at the crack tip. It concluded that film rupture and anodic dissolution at a slip steps was the operating mechanism of scc under high anodic polarization condition. The curves pertaining to the α-Al bronze system under anodic potentials (as in Fig. 8) show a decrease of current with time caused by the formation of a protective oxide layer. Recently, two mechanisms have been proposed to explain the scc of Cu-base alloys. One is the mechano-chemical model including film rupture [11, 27–29]. The other is a dealloying or selective dissolution model [30–35]. According

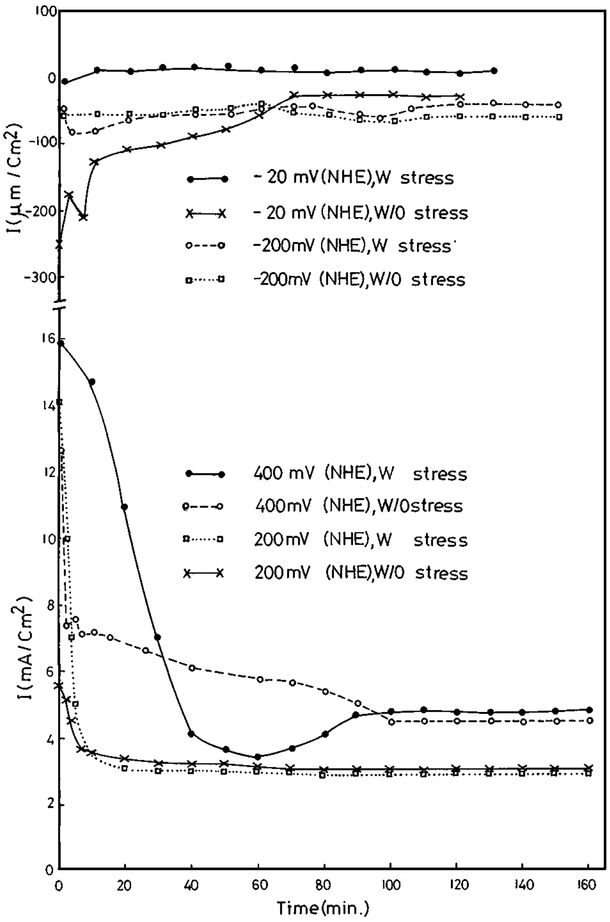


Figure 8 Effect of potential on current-time curves of α-Al bronze in 3.4% NaCl + 20 ppm Na_2S with (w) and without (w/o) stress.

to the first mechanism, the break down of the oxide film on the α-Al bronze surface takes place and the surface of the alloy becomes relatively active. The interaction of the applied stress with the oxide film leads to the formation of a slip step that causes the rupture of the film. It has been proposed [23], for 90 Cu-10 Ni alloy in seawater polluted by sulfide ions, that film rupture occurrs and two scc mechanisms are operational, namely sulfide stress cracking associated with anodic dissolution in the low sulfide concentration range (less than 100 ppm) and hydrogen embrittlement, which is dominant in the high sulfide concentration range (more than 100 ppm). It was found that a synergism exists between sulfide and stress that enhances the effect of the latter [23].

The results of tests indicate that α-Al bronze in 3.4% NaCl with sulfide contamination under OCP or cathodic potentials was less susceptible to scc compared to when the alloy was anodically polarized.

4. Conclusions

1. The results of scc measurements and metallographic observations indicate that α-Al bronze in 3.4% NaCl + 20 ppm Na_2S is mildly susceptible to scc at the higher potentials ($\geq$200 mV_{NHE}).

2. The susceptibility of α-Al bronze to scc depends on the sulfide ion concentration in the saline water and the anodic potential, which increases the severity attack.

3. The increase of sulfide ions in polluted saline water leads to a reduction in the maximum stress (σ max) and changes the morphology of the fracture surface from ductile to brittle at anodic potentials.

4. The results support film rupture and anodic dissolution at slip steps as the operating mechanism.

References

1. E. G. WEST, "Copper and it's Alloys" (Ellis-Hardwood Ltd., New York, 1982) p. 155.
2. R. B. ROSS, "Metalic Materials Specification Handbook," 3rd ed. (E. and F.N.Spon, London, 1968) p.139.
3. P. J. MAKIN and A. A. SMITH, "The Aluminium Bronzes," 2nd ed. (Copper Development Association, London, 1966).
4. Aluminium bronze alloy technical data, Copper Development Association, Potters Bar, 1982.
5. Z. AHMED, *Brit. Corros. J.* **11** (1976) 149.
6. H. LEIDHEISER, JR, "The Corrosion of Copper, Tin and their Alloys" (John Wiley & Sons, Inc., New York, 1971) p. 82.
7. F. L. LAQUE, "Marine Corrosion" (John Wiley & Sons, Inc., New York 1975) p. 223.
8. C. MANFREDI, S. SIMPSON and S. R. DE SANCHEZ, *Corrosion* **43** (1987) 458.
9. B. G. ATEYA, E. A. ASHOUR and S. M. SAYED, *J. Electrochem. Soc.* **141** (1994) 71.
10. T. H. ROGERS, "Marine Corrosion" (George Newnes Pub. Co., London, 1968) p. 124.
11. M. ISLAM, in Proceedings of the 9nd International Conference on Mettalic Corrosion, held in Toronto, Canada, 1984, p. 161.
12. D. H. THOMPSON, *Mater. Res. Std.* **1** (1961) 108.
13. B. G. ATEYA, E. A. ASHOUR and S. M. SAYED, *Corrosion* **50** (1994) 20.
14. E. A. ASHOUR, in 2nd Alexandria International Conference on Heat Exchangers, Boilers and Pressure Vessels, 22–23 April 1995, Vol. 1, p. 65.
15. F. RICHARDS, "Chemical Oceanography" (Academic Press, Inc., New York 1965) p. 611
16. J. F. BATES and J. M. POPPLEWELL, *Corrosion* **31** (1975) 269.
17. R. SANCHEZ and D. J. SCHIFFRIN, *Corrosion Sci.* **22** (1982) 585.
18. C. KATO, H. W. PICKERING and J. E. CASTLE, *J. Electrochem. Soc.* **131** (1984) 1225.
19. J. P. GUDAS and H. P. HACK, *Corrosion* **35** (1979) 67.
20. J. N. ALHAJJI and M. R. REDA, *J. Electrochem. Soc.* **141** (1994) 1432.
21. *Idem., ibid.* **142** (1995) 2944.
22. B. C. SYRRETT, *Corrosion Sci.* **21** (1981) 187.
23. A. EL-DOMIATY and J. N. ALHAJJI, *J. of Materials Engineering and Performance* **6** (1997) 534.
24. E. A. ASHOUR and E. A. ABD EL MEGUID and B. G. ATEYA, *Corrosion* **53** (1997) 612.
25. D. TROMANS and R. H. SUN, *J. Electrochem. Soc.* **138** (1991) 3235.
26. A. SCHUSSLER and H. E. EXNER, *Corrosion Sci.* **34** (1993) 1793.
27. D. J. DUQUETTE, *Corrosion* **46** (1990) 434.
28. M. G. ALVAREZ, C. MANFREDI, M. GIORDANO and J. R. GALVELE, *Corrosion Sci.* **24** (1984) 769.
29. R. B. REBAK, R. M. GARANZA and J. R. GALVELE, *ibid.* **28** (1988) 1089.
30. H. LEIDHEISER and R. KISSINGER, *Corrosion* **28** (1972) 218.
31. T. K. G. NAMBOODHIRI and R. S. TRIPATHI, *Corrosion Sci.* **26** (1986) 745.
32. H. W. PICKERING, *ibid.* **23** (1983) 1107.
33. A. PARTHASARLI and N. W. POLAN, *Corrosion* **43** (1987) 12.
34. H. KAISER, in "Alloy Dissolution, in Corrosion Mechanisms," edited by F. Mansfeld (Marcel Dekker, New York, 1987) p. 85.
35. G. T. BURSTEIN and G. GAO, *J. Electrochem. Soc.* **141** (1994) 912.

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