PII: S0010-938X(97)00111-X

A COMPARATIVE STUDY OF THE PASSIVATION AND LOCALIZED CORROSION OF α -BRASS AND β -BRASS IN BORATE BUFFER SOLUTIONS CONTAINING SODIUM CHLORIDE: III. THE EFFECT OF TEMPERATURE

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Abstract—The passivation and localized corrosion of α -brass and β -brass in an aqueous borate–boric acid buffer (pH 9) containing different concentrations of NaCl (c_{NaCl}) in the temperature range $5^{\circ}\text{C} \leq T \leq 45^{\circ}\text{C}$ were studied comparatively by potential sweeping at $2 \times 10^{-2} \text{ V s}^{-1}$ and $2 \times 10^{-4} \text{ V s}^{-1}$ and de-alloying measurements. The passivation of α -brass and β -brass was related to the electroformation of a complex $\text{ZnO} \cdot x\text{H}_2\text{O}/\text{Cu}_2\text{O}$ layer, its thickness and compactness presumably increasing with temperature. For both α -brass and β -brass immersed in an aqueous NaCl-containing buffer, pitting corrosion was observed as the value of the breakdown potential (E_b) was exceeded. At constant temperature, the value of E_b shifted negatively as either c_{NaCl} or the zinc content in the alloy was increased. For β -brass, the value of E_b decreased slightly with increasing temperature in the range $5^{\circ}\text{C} \leq T \leq 45^{\circ}\text{C}$. In the range $5^{\circ}\text{C} \leq T \leq 25^{\circ}\text{C}$, for α -brass the value of E_b was close to that reported for copper, whereas for $T > 25^{\circ}\text{C}$ it approached those values measured for β -brass. De-alloying measurements in aqueous 0.5 M NaCl indicate that zinc surface enrichment of α -brass was responsible for the decrease in pitting corrosion resistance at $T > 45^{\circ}\text{C}$. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: A. brass, C. passive films, C. localized corrosion.

INTRODUCTION

The electrochemical behaviour of Cu–Zn alloys (brass) has been studied extensively over a wide range of experimental conditions in relation to dezincification and stress corrosion cracking^{1–3} and, more recently, passivation and pitting corrosion.^{4–6} In neutral and alkaline solutions the passivation of brass involves the electroformation of a complex $\text{ZnO} \cdot x\text{H}_2\text{O}$ and Cu_2O layer, as concluded from electrochemical, X-ray photoelectron spectroscopy and Auger spectroscopy data.⁷ In general, passivity breakdown depends strongly on the composition of the alloy, the aggressive environment and temperature.

The breakdown potential (E_b) of α -brass, β -brass and $\alpha + \beta$ -brass in chloride-containing

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Manuscript received 3 May 1997

buffers shifts negatively as the Cu/Zn ratio in the alloy decreases,⁶ although E_b is hundreds of mV more positive than that of zinc owing to the formation of a copper-enriched surface layer.⁶ On the other hand, the increase in NaCl concentration (c_{NaCl}) produces a substantial decrease in the potential range of passivity, promoting pitting corrosion.⁶ However, in contrast to other metals and alloys, little is known about the influence of temperature on the passivation and pitting corrosion of brass.

This work refers to a comparative study of the passivation and pitting corrosion of α -brass and β -brass in an aqueous NaCl-containing borate-boric acid buffer in the temperature range $5^\circ\text{C} \leq T \leq 45^\circ\text{C}$. At a given NaCl concentration, the value of E_b for β -brass decreases slightly as the temperature is increased. For α -brass, in the range $5^\circ\text{C} \leq T \leq 25^\circ\text{C}$, the value of E_b is close to that reported previously for copper;⁸ for $T > 25^\circ\text{C}$ it diminishes, approaching that observed for β -brass. This fact can be explained by the enhancement of electrodisolution of copper from the alloy as the temperature is increased above 25°C .

EXPERIMENTAL METHOD

Working electrodes (specimens) were made from rods of α -brass and β -brass, with the following chemical composition: 71.719% Cu, 28.228% Zn, 0.011% C, 0.008% Al, 0.031% Sn, 0.001% As for α -brass, and 54.700% Cu, 45.240% Zn, 0.026% C, 0.005% Al, 0.023% Sn, As and Si < 0.001 for β -brass.

Brass rods were made by melting and casting known amounts of copper (99.999%) and zinc (99.999%). Drawn brass bars 0.6 cm in diameter were machined to obtain cylindrical specimens 0.3 cm in diameter. Specimens were mounted vertically and the base of each cylinder was used as a horizontal disc working electrode in contact with a hanging column of the electrolyte solution.⁹ The working electrode (specimen) was wet polished with emery papers of different grain size and finished with $1\ \mu\text{m}$ grit alumina paste. Subsequently, each specimen was cleaned ultrasonically, rinsed successively with distilled acetone and doubly distilled water, and dried in air at room temperature. Finally, specimens were lodged under argon in Pyrex tubing, and thermally treated at 150°C for 2 h to eliminate residual mechanical stresses and improve surface uniformity. This pretreatment led to good reproducibility of the results.

Electrochemical runs were made in quiescent aqueous $0.075\ \text{M}\ \text{Na}_2\text{B}_4\text{O}_7 + 0.15\ \text{M}\ \text{H}_3\text{BO}_3$ (pH 9), with and without the addition of aqueous $x\ \text{M}\ \text{NaCl}$ ($0.05 \leq x \leq 0.5$), covering the temperature range $5^\circ\text{C} \leq T \leq 45^\circ\text{C}$. Occasionally, solutions under stirring conditions were employed to explore possible diffusion-controlled processes from the solution side. A conventional three-electrode Pyrex glass cell was used including the specimen, the reference electrode and a platinum wire counter electrode. The potential applied to the working electrode was measured against a saturated calomel electrode (SCE) provided with a Luggin-Haber capillary tip. All potentials in the text are referred to the saturated calomel electrode at $T = 25^\circ\text{C}$. For this purpose, the following equation was employed⁸

$$E/V = 0.2421 - 6.61 \times 10^{-4}(T - 25) - 1.75 \times 10^{-6}(T - 25)^2 \quad (1)$$

Conventional triangular potential sweep voltammetry was run at $v = 2 \times 10^{-2}\ \text{V s}^{-1}$ and at $v = 2 \times 10^{-4}\ \text{V s}^{-1}$ starting from the cathodic switching potential, E_{cs} , to the anodic switching potential, E_{as} . At the lowest value of v , the behaviour of voltammograms closely approached that of potentiostatic polarization curves.

The amount of soluble species produced during the anodic polarization of specimens was determined by atomic absorption spectroscopy.

EXPERIMENTAL RESULTS AND INTERPRETATION

Voltammetric data of α -brass and β -brass in a NaCl-free boric buffer

Voltammograms run with α -brass specimens at different temperatures between E_{cs} and E_{as} (Fig. 1) exhibit peaks A1 and A1' at -1.2 V and -0.75 V, respectively, related to electroformation of $ZnO \cdot xH_2O$, and peaks C1 at -1.3 V and C1' at -0.90 V related mainly to the electroreduction of $ZnO \cdot xH_2O$ and partly to the electroreduction of $Zn(II)$

Fig. 1. Voltammograms of α -brass in a borate-boric acid buffer run at 0.02 V s^{-1} at different temperatures.

soluble species produced in the preceding half-cycle in the potential range of peaks AI–AI'.^{6,10}

The contribution of the electroformation of Cu₂O species to the anodic layer can be observed when the applied potential (E) exceeds -0.25 V, i.e. in the region of peak AII,^{6,11} whereas the electro-oxidation of Cu₂O to CuO takes place at $E > 0.25$ V. Otherwise, the electroreduction of CuO to Cu₂O occurs in the range $-0.25 \text{ V} > E > -0.40$ V (peak CII), whereas the electroreduction of Cu(I) species to Cu occurs in the range $-0.5 \text{ V} > E > -0.8$ V (peak CII'), overlapping to some extent the electroreduction of Zn(II) species at CI'.

The overall voltammetric charge (q), particularly that involved at low values of E , increases with temperature. From these voltammograms it can be concluded that the anodic layer formed at $E > -0.25$ V consists of copper oxides and ZnO· x H₂O. It should be noted that the value of x determining the water content of the zinc oxide layer decreases as temperature is increased, as the Zn(OH)₂ species is easily dehydrated approaching the ZnO stoichiometry.¹²

Solution stirring produces no marked changes in the above mentioned voltammograms, at least in the potential range of peaks AI–AI' and CI–CI'. Therefore, the electrochemical reactions associated with these peaks can be principally assigned to the processes taking place on the specimen surface, either solid phase formation or disappearance, respectively. Then, for $E > -0.7$ V, the voltammetric electro-oxidation charge is largely stored as a ZnO· x H₂O layer on α -brass. The decrease in the anodic current at $E > -0.5$ V is related to the increase in average thickness of the ZnO· x H₂O layer.

The preceding description is qualitatively similar for all voltammograms run in the range $5^\circ\text{C} \leq T \leq 45^\circ\text{C}$. From a quantitative standpoint, on increasing temperature, current peaks are better defined and the corresponding charges are increased. In this case, the contribution of the background current related to electrodeposition of zinc at $E < -1.0$ V can also be observed.

Voltammograms of β -brass specimens in either still or stirred solutions run in the same range of temperature (Fig. 2) are qualitatively similar to those described above for α -brass, although for β -brass the formation and electroreduction charges involving Zn(OH)₂ and Zn(II)-containing species are relatively greater than the charge involved in the electroreduction and electroformation of copper oxide species.

Similarly to α -brass, the shape of the voltammetric profiles for β -brass does not change appreciably on increasing the temperature, although a net increase in the voltammetric charge related to the electroformation and electroreduction of zinc and copper oxides can be observed. This fact suggests that the anodic layer becomes thicker or more compact on increasing the temperature.

Voltammetric data from NaCl-containing borate buffers

Voltammograms of α -brass (Fig. 3) and β -brass (Fig. 4) were run at different temperatures in an aqueous 0.5 M NaCl-containing buffer covering values of E_{as} lower than E_b to avoid the interference of pitting corrosion in the electroformation of the anodic layer. Processes related to the electroformation and electroreduction of ZnO· x H₂O and soluble ZnCl₄²⁻ species are clearly observed in the potential range $-1.2 \text{ V} \leq E \leq E_b$. As these voltammograms are similar to those observed for the plain buffer, it appears that in this case the anodic layer also consists of a ZnO· x H₂O layer on a copper-enriched surface. Accordingly, as observed in the plain borate–boric acid buffer, the

Fig. 2. Voltammograms of β -brass in a borate-boric acid buffer run at 0.02 V s^{-1} at different temperatures.

increase in temperature in this case results in the charge increase of peaks AI and AI' which are related to the electroformation of $\text{ZnO} \cdot x\text{H}_2\text{O}$ and Zn(II) soluble species.

Pitting corrosion potential measurements

For both α -brass and β -brass, values of E_b were determined from anodic polarization curves recorded from -1.3 V upwards at $v = 2 \times 10^{-4} \text{ V s}^{-1}$ in a buffer solution containing either $5 \times 10^{-2} \text{ M}$ NaCl or 0.5 M NaCl, covering the range $5^\circ\text{C} \leq T \leq 45^\circ\text{C}$ (Fig. 5). The value of E_b was defined as the most positive potential where the anodic current still remains in the 'passivity range'. The polarization curve for α -brass recorded at 5°C comprises the formation of a rather smaller amount of Zn(II) species, and a relatively larger amount of Cu(II) species. Furthermore, in this case, the value of E_b is more positive than that observed for β -brass. When temperature is increased from 5°C to

Fig. 3. Voltammograms of α -brass in a 0.5 M NaCl-containing borate-boric acid buffer run at 0.02 V s^{-1} at different temperatures.

Fig. 4. Voltammograms of β -brass in a 0.5 M NaCl-containing borate-boric acid buffer run at 0.02 V s^{-1} at different temperatures.

Fig. 5. Anodic polarization curves of α -brass and β -brass in a 0.5 M NaCl-containing borate-boric acid buffer run at $2 \times 10^{-4} \text{ V s}^{-1}$ and different temperatures.

45°C, the values of E_b for both α -brass and β -brass move negatively, although at 45°C, the values of E_b for both specimens tend to be very close to each other. However, as usually observed for other systems,¹³ the values of E_b are scattered in a rather broad

potential range so that a statistical analysis of E_b is needed. In this case, it is useful to define the probability ($P_n \geq 1$) of forming at least one stable pit at the potential E , as:¹³

$$P_n \geq 1 = N(E)/N_t \quad (2)$$

where $N(E)$ is the number of specimens that develop pitting at a given E in the pitting potential range, and N_t is the total number of specimens. The cumulative ($P_n \geq 1$) vs. E plots derived from the anodic polarization curves for α -brass and β -brass in aqueous NaCl-containing buffers at 5°C and 45°C (Fig. 6) indicate that the range of potential related to pitting corrosion becomes relatively broad and shifts positively as either the copper content in the alloy is increased or c_{NaCl} is diminished. On the other hand, for α -brass, at a constant c_{NaCl} , the value of E_b decreases slightly in the range 5°C $\leq T \leq 25^\circ\text{C}$,

Fig. 6. $P_n \geq 1$ vs. E plots resulting from polarization curves for α -brass and β -brass in a NaCl-containing borate-boric acid buffer at different NaCl concentrations: (a) $T = 5^\circ\text{C}$; (b) $T = 45^\circ\text{C}$.

Fig. 7. $P_n \geq 1$ vs. E plots resulting from polarization curves of α -brass in a 0.05 M NaCl-containing borate-boric acid buffer at different temperatures.

whereas it exhibits a substantial decrease for $T > 25^\circ\text{C}$ (Fig. 7). For β -brass the value of E_b remains practically constant in the range $5^\circ\text{C} \leq T \leq 25^\circ\text{C}$, and decreases slightly for $T > 25^\circ\text{C}$, irrespective of c_{NaCl} .

If the average pitting potential value ($\langle E_b \rangle$) is that corresponding to $P_n \geq 1 = 50\%$, a plot of $\langle E_b \rangle$ vs. T for both α -brass and β -brass in aqueous 0.5 M and 0.05 M NaCl-containing buffers (Fig. 8) enables values of $\langle E_b \rangle$ to be compared with those resulting from polycrystalline copper and zinc specimens in the same solutions. These plots clearly show that for α -brass the value of E_b lies close to that of copper⁸ only in the range $5^\circ\text{C} \leq T \leq 25^\circ\text{C}$, but it is definitely much smaller for $T > 25^\circ\text{C}$. For β -brass, $\langle E_b \rangle$ remains nearly the same in the range $5^\circ\text{C} \leq T \leq 25^\circ\text{C}$, and approaches that of α -brass for $T > 25^\circ\text{C}$. Otherwise, for β -brass, at constant temperature, the value of $\langle E_b \rangle$ is always more negative than that for copper in the same solution because of the low copper content in β -brass. In any case, the value of $\langle E_b \rangle$ is hundreds of mV more positive than the value of $\langle E_b \rangle$ for polycrystalline zinc in the range of temperature covered by this work.

It is interesting to note that the difference between $\langle E_b \rangle$ values of α -brass and β -brass tends to disappear at 45°C , i.e. α -brass behaves as an alloy with low copper content. In principle, this can be related to changes in the surface composition of the alloy produced at this temperature during alloy electrodisolution.

De-alloying of α -brass and β -brass in 0.5 M NaCl at different temperatures

The anodic polarization curves of α -brass and β -brass in 0.5 M NaCl at 5°C and 45°C (Fig. 9) exhibit a broad potential region where Zn(II) soluble species are produced through a thin $\text{ZnO} \cdot x\text{H}_2\text{O}$ layer.¹⁴ At constant temperature, this potential region moves positively as the zinc content in the alloy decreases, whereas the electrodisolution current increases with temperature. The selective electrodisolution of zinc extends from

Fig. 8. E_b vs. T plots for α -brass, β -brass, copper and zinc in a borate-boric acid buffer containing different NaCl concentrations.

$E \cong -1.1$ V to -0.4 V, whereas the simultaneous electrodisolution of both zinc and copper takes place from $E > -0.4$ V,¹⁴ producing a considerable increase in current.

Polarization curves clearly indicate that in the potential range where pitting corrosion of α -brass and β -brass is observed in the aqueous NaCl-containing buffer, the electrodisolution of both components produces changes in the surface composition of the alloy which can be followed by the determination of dissolved copper and zinc.

Atomic absorption measurements

The preferential electrodisolution of zinc was achieved by holding the specimens for 3 h at $E = 0.0$ V in aqueous 0.5 M NaCl at different temperatures, the amounts of soluble copper and zinc species subsequently being determined by atomic absorption spectroscopy analysis. These results are shown in Table 1.

Results assembled in Table 1 indicate that, in the range $5^\circ\text{C} \leq T \leq 25^\circ\text{C}$, α -brass in aqueous 0.5 M NaCl undergoes milder corrosion than β -brass, but for $T = 45^\circ\text{C}$ the corrosion behaviour of α -brass in this solution approaches that of β -brass.

For both alloys, the Cu/Zn ratio in the solution remains constant in the range

Fig. 9. Anodic polarization curves recorded at $2 \times 10^{-4} \text{ V s}^{-1}$ for α -brass and β -brass in aqueous 0.5 M NaCl: (a) $T = 5^\circ\text{C}$; (b) $T = 45^\circ\text{C}$.

$5^\circ\text{C} \leq T \leq 25^\circ\text{C}$, but it increases markedly for $T > 25^\circ\text{C}$. The relatively higher level of copper species in solution for α -brass, as compared with β -brass at 45°C , implies zinc enrichment at the surface of α -brass during electrodisolution. This fact can explain the decrease in pitting corrosion resistance of α -brass at this temperature.

Table 1. Concentration (c) of soluble Cu and Zn species and Cu/Zn concentration ratio (r) resulting from the anodic polarization of specimens at $E = 0.0$ V for 3 h in aqueous 0.5 M NaCl, at different temperatures

	T ($^{\circ}\text{C}$)		
	5	25	45
α -brass			
c_{Cu} (ppm)	0.15	0.19	1.1
c_{Zn} (ppm)	5.5	7.7	23.1
$r(\text{Cu/Zn})$	0.027	0.025	0.048
β -brass			
c_{Cu} (ppm)	0.14	0.16	0.54
c_{Zn} (ppm)	12.23	17.8	25.12
$r(\text{Cu/Zn})$	0.011	0.009	0.021

The physical picture underlying these results can be summarized as follows. The anodic layers produced on both α -brass and β -brass are almost similar in nature in the range $5^{\circ}\text{C} \leq T \leq 45^{\circ}\text{C}$. When local rupture of the anodic layer takes place in the range $5^{\circ}\text{C} \leq T \leq 25^{\circ}\text{C}$, α -brass exhibits a surface layer richer in copper than that of β -brass. But for $T > 25^{\circ}\text{C}$, the surface composition of both alloys tends to be the same. Then, except for the observations made in the lower temperature range, the resistance to pitting corrosion of α -brass and β -brass becomes very similar.

CONCLUSIONS

- (1) In the range $5^{\circ}\text{C} \leq T \leq 45^{\circ}\text{C}$, the passive layers formed on α -brass and β -brass in plain borate-boric acid buffer and in NaCl-containing buffer behave similarly, although the average anodic layer thickness produced under preset voltammetric conditions increases slightly with the temperature.
- (2) At constant temperature and NaCl concentration, the value of E_b increases with the Cu/Zn ratio in the alloy.
- (3) For β -brass, the value of E_b remains almost constant in the range $5^{\circ}\text{C} \leq T \leq 25^{\circ}\text{C}$, and decreases slightly for $T > 25^{\circ}\text{C}$.
- (4) For α -brass, the value of E_b is almost constant or decreases slightly in the range $5^{\circ}\text{C} \leq T \leq 25^{\circ}\text{C}$ remaining close to those E_b values already reported for copper. Otherwise, for $T > 25^{\circ}\text{C}$, the value of E_b decreases to those values observed for β -brass.
- (5) The comparable pitting corrosion behaviour of α -brass and β -brass in NaCl-containing buffer at $T > 25^{\circ}\text{C}$ can be explained by the decrease in the Cu/Zn ratio at the surface of the α -brass.

Acknowledgements—R.C.S. and A.J.A. thank DGCYCT (Spain) and CONICET (Argentina) for financial support. The authors also thank UNELCO S.A. (Canary Islands) for partial financial support.

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