região entre a dupla camada e o pico C, a adsorção específica na região do óxido, e ainda o facto de ClO_4^- ser menos fortemente adsorvido que os iões HSO_4^-/SO_4^{2-}.

Postula-se ainda que a espécie percursora do pico C é $Ir(OH)_3$ e que o papel dos aniões se traduz numa indução do fenómeno de oxidação, facilitando a transição $Ir(III) \rightarrow Ir(IV)$ (pico D).

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ELECTROCHEMICAL BEHAVIOUR OF (α-β) BRASS IN BORATE BUFFER SOLUTIONS CONTAINING SODIUM CHLORIDE. INFLUENCE OF TEMPERATURE

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ABSTRACT

The passivation and localized corrosion of (α-β) brass is studied in borate-boric acid buffer + 0.5 M NaCl aqueous solution (pH 9) in the 0 - 60 °C range using electrochemical techniques combined with surface microscopy. Passivation of α-β brass in borate-boric acid buffer is due to the electroformation of a complex $ZnO.xH_2O$ and $Cu_2O/CuO/Cu(HO)_2$ anodic layer. In borate-boric acid buffer + 0.5 M NaCl passivity breakdown leading to pitting corrosion is observed when the applied potential exceeds E_b, the breakdown potential. The E_b vs T plot gives a straight line with slope -5×10^{-3} V/°C. At a constant T the localized corrosion resistance of α-β brass results considerably lower than that of polycrystalline Cu.

INTRODUCTION

Corrosion and passivation of Cu have been extensively considered over the past years (1). Passivation in aqueous alkaline solutions involves the initial formation of a Cu_2O monolayer, and as the applied potential is moved positively, an anodic layer consisting of an inner Cu_2O and an outer hydrous CuO layer is formed (2). The electrochemical behaviour of the passive layer depends considerably on the solution composition and temperature (3). The presence of aggresive anions such as Cl^-, Br^- and SO_4^{2-} in the solution assists the localized corrosion of Cu when the applied potential exceeds a certain critical value E_b (4-6). Pitting corrosion of Cu in borate-boric acid buffer containing NaCl in the 0 - 70 °C range showed a complex dependence of E_b on temperature T (4). Thus, in the 0 - 20 °C range, E_b decreased as T was increased, whereas in the 20 - 70 °C range the opposite dependence was found (4).

The available information on passivation and pitting corrosion of (α-β) brass in moderate alkaline aqueous solution are much scarce as compared to that on Cu (7).

In this paper the pitting corrosion of $(\alpha-\beta)$brass in borate- boric acid buffer containing 0.5 M NaCl in the 0 °C < T < 60 °C range is studied using conventional electrochemical techniques complemented with optical microscopy.

EXPERIMENTAL

Working electrodes were made from $(\alpha-\beta)$ brass rods (DIN 8513 L, 0.3 cm dia, chemical composition 60.0% Cu, 39.3% Zn, 0.2% Si, 0.3% Sn, 0.2% Mn). The working electrode was a disc (base of cylindrical specimens) in contact with a hanging electrolyte column. Each working electrode was mechanically polished and thermally treated at 150 °C during 2 hs to eliminate residual mechanical stresses and to make the surface characteristics more uniform.

Polarizartion curves at v = 0.02 V/s and v = 2x10^{-4} V/s were made in a conventional three- electrodes Pyrex glass cell in the 0 °C < T < 60 °C range. Potentials were measured against a saturated calomel electrode (SCE). A platinum wire was used as counterelectrode.

RESULTS AND DISCUSSION

The current density (j) vs potential (E) plots of $(\alpha-\beta)$ brass in the borate-boric acid buffer run at 0.02 V/s and 25 °C show anodic current peaks A_1, A_1' and A_2, and cathodic peaks C_1, C_2', C_2'', and C_2 (Fig.1). Peaks A_1 (-1.1 V) and A_1' (-0.8 V), can be assigned to the Zn electrooxidation yielding ZnO.xH$_2$O and soluble species as these peaks are observed for Zn in borate-boric acid buffer (8).

At potentials more positive than -0.7 V the anodic current decreases due to the growth of the ZnO.xH$_2$O layer (8). The ZnO.xH$_2$O layer is electroreduced to Zn in the potential region of peak C_1 (-1.25 V). Broad anodic peak A_2

Fig. 1 Current density (j)-potential (E) profile (first scan) for the $(\alpha-\beta)$ brass at 0.02 V/s in the borate-boric acid buffer at 25°C.

(-0.05 V) which is observed for polycrystalline Cu in borate-boric acid buffer (5) corresponds to the electroformation of a Cu$_2$O layer and its further electrooxidation to a Cu$_2$O/CuO/Cu(HO)$_2$ complex layer (2-5). On the other hand, the constant anodic current observed at potentials more positive than 0.3 V is due to passive layer growth and metal electrodissolution through the passive layer (2,5). Finally, Peak C''$_2$ (-0.35 V) is related to CuO/Cu(OH)$_2$ layer electroreduction yielding Cu$_2$O, whereas peaks C$_2'$ (-0.68 V) and C$_2$ (-1.0 V) correspond to Cu$_2$O electroreduction to Cu (2,5).

Micrographs of $(\alpha-\beta)$ brass surface after cycling at 0.02 V/s (Fig. 2) show two different regions, the corrosion-free α-phase (white regions) amd the β-phase (dark regions) which presents a preferential dezincification. No pits are detected on $(\alpha-\beta)$ brass surface.
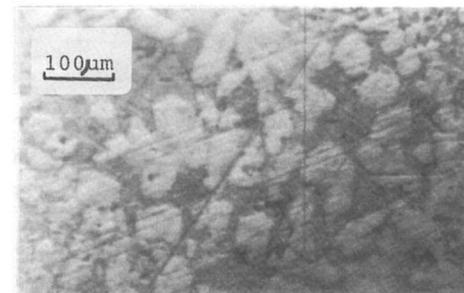
Fig. 2 Micrograph of the $\alpha-\beta$ brass surface after the J/E runs at 0.02 V/s in the borate-boric acid buffer at 25°C.

The anodic polarization curves of $(\alpha-\beta)$ brass in the borate-boric acid +0.5 M NaCl at started from -0.6 V at ω = 2 10^{-4} V/s in the 0°C < T < 60°C range show peak A_2 followed by a passive region which extends up to a certain critical potential E_b. At potentials more positive than E_b a remarkable anodic current increase is observed (Fig. 3). Micrographs of $(\alpha-\beta)$ brass after this anodic polarization reveal that the current increase should be related to the nucleation and growth of pits on $(\alpha-\beta)$ brass surface (Fig. 4).
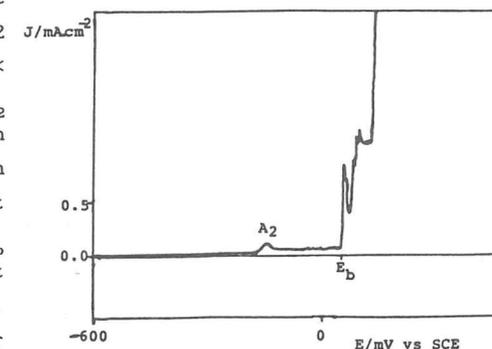
Fig. 3 Anodic polarization curve at v = 2.10^{-4} V/s in the borate-boric acid buffer containing 0.5 M NaCl at 25°C.

Pits are not observed when the anodic polarization limit is restricted to potential values more negative than E_b.
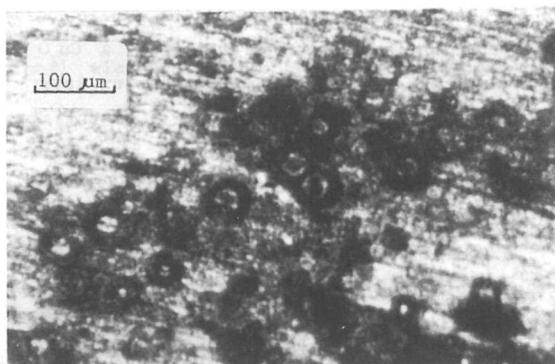
Fig. 4 Micrograph of the $(\alpha-\beta)$ brass surface after the anodic polarization curves run at $\omega = 2 \cdot 10^{-4}$ V/s in the borate-boric acid buffer containing 0.5 M NaCl at 25° C.

Nucleation and growth of pits take place preferentially at grain boundaries which are richer in Zn, and accordingly, more reactive. The dynamics of pit nucleation and growth involves current bursts due to the birth and death of pits.

The E_b values derived from the j vs E curves move negatively as T is raised. The E_b vs T plot gives a straight line with slope $-5 \times 10^{-3} \pm$ V/°C (Fig. 5). The dependence of E_b on T for $(\alpha-\beta)$ brass differs drastically from that observed for polycrystalline Cu under comparable conditions (4). This difference in temperature dependence of E_b reflects the different composition and properties variation with temperature of the corresponding passive layers. The passive layer produced on $(\alpha-\beta)$ brass is less protective than that formed on polycrystalline Cu as E_b values for $(\alpha-\beta)$ brass are more negative than those of polycrystalline Cu.

Fig. 5 E_b vs T plot. Borate-boric acid + 0.5 M NaCl

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