JOURNAL OF APPLIED ELECTROCHEMISTRY **23** (1993) 1280–1284

Electrochemical passivation of copper–aluminium–silver alloy in sodium hydroxide solution

M. ANBU KULANDAINATHAN, S. VENKATAKRISHNA IYER*

Central Electrochemical Research Institute, Karaikudi 623 006, India

R. SURESH BABA, T. VASUDEVAN

Department of Industrial Chemistry, Alagappa University, Karaikudi 623 004, India

Received 10 November 1992; revised 23 March 1993

The effect of consecutive cyclic polarization of a new heat treated and mechanically polished Cu–Al–Ag alloy of entirely new composition with a high aluminium content on the surface microstructure has been studied using scanning electron microscopy and X-ray diffractometry. The electrochemical behaviour of this alloy in 0.5 M NaOH has been studied using cyclic voltammetry and impedance measurements. Repetitive triangular sweeps (RTPS) potential scans between hydrogen and oxygen evolution in alkaline media lead to preferential dissolution of the aluminium. The steady state *I–E* profile of the alloy after the RTPS pretreatment indicates surface dealloying of aluminium due to its preferential dissolution, and shows a characteristic similar to that for high purity copper and silver.

---

1. Introduction

Of the many shape memory alloys, only Ni–Ti and copper-based alloys have been proved to be commercially viable, having useful engineering properties [1]. These alloys have some practical interest mainly in electronics, odontology, ornaments and dentistry. The three commercially viable copper based alloy systems are Cu–Zn–Al, Cu–Al–Ni and Cu–Al–Ag. Cu–Al–Ag alloys are regarded as promising new materials, because of their good mechanical properties, conductivity, appearance [2], high corrosion resistance [2, 3] and ease of preparation. The mechanical properties and equilibrium diagrams of Cu–Al–Ag alloys have been well studied [4, 5]. However, only a few studies have been reported on the electrochemical behaviour of these alloys in different media [6–8]. Recent studies have shown that Cu (89.4%), Al (10.5%) and Ag (10%) alloy has a very low corrosion rate in artificial saliva [5]. The potentiodynamic behaviour of this alloy in deaerated 0.5 M NaOH solution at 30° C was also examined [9]. After the application of a repetitive triangular potential scan to the alloy, between hydrogen and oxygen evolution, the gradual achievement of a stabilized *I–E* profile with the absence of aluminium on the surface due to its preferential dissolution, was observed. Such stabilized *I–E* profiles were interpreted to be the result of additive effects of pure copper and silver nuclei formed on the alloy surface, since copper and silver oxidation and reduction processes take place in different potential ranges (surface dealloying) and no differences in the number of peaks and peak potentials were observed while changing the alloy composition and heat treatment.

In the present study a new, less expensive, Cu–Al–Ag alloy of different composition containing more aluminium was cast, heat treated and reformed by repetitive triangular potential scanning. Its electrochemical behaviour and surface characteristics were studied using cyclic voltammetry, impedance spectroscopy, atomic absorption spectroscopic analysis, SEM and XRD, and finally, its behaviour was compared with that of high purity alloying metals.

2. Experimental details

Cylindrical rods of the alloy were prepared using copper, aluminium and silver of 99.9% purity as described elsewhere [6]. The alloy composition was determined by atomic absorption spectroscopy using a Perkin–Elmer machine (model 380) using air–acetylene and nitrous oxide–acetylene flames. The composition of the alloy was Cu–Al(19%)–Ag(19%). The spectroscopic analysis showed the presence of Si(0.038%), Fe(0.53%), Zn(0.01%) and Mg(0.018%). The alloy was annealed at 500° C to attain equilibrium structure. The working electrode was embedded in a Teflon rod to expose only the base of the cylinder to the electrolyte. The exposed base of the alloy cylinder was oriented vertically to permit the dislodging of gas bubbles from the electrode. The exposed electrode area was 0.48 cm^2. The potential of the working electrode was measured against a Hg|HgO|OH$^-$ electrode in the same solution. The counter electrode was a platinum sheet of large area.

Experiments were performed in a conventional cell at 27° C using pre-electrolysed 0.5 M NaOH solution.

---

[*] Author to whom all correspondence should be addressed.

0021-891X

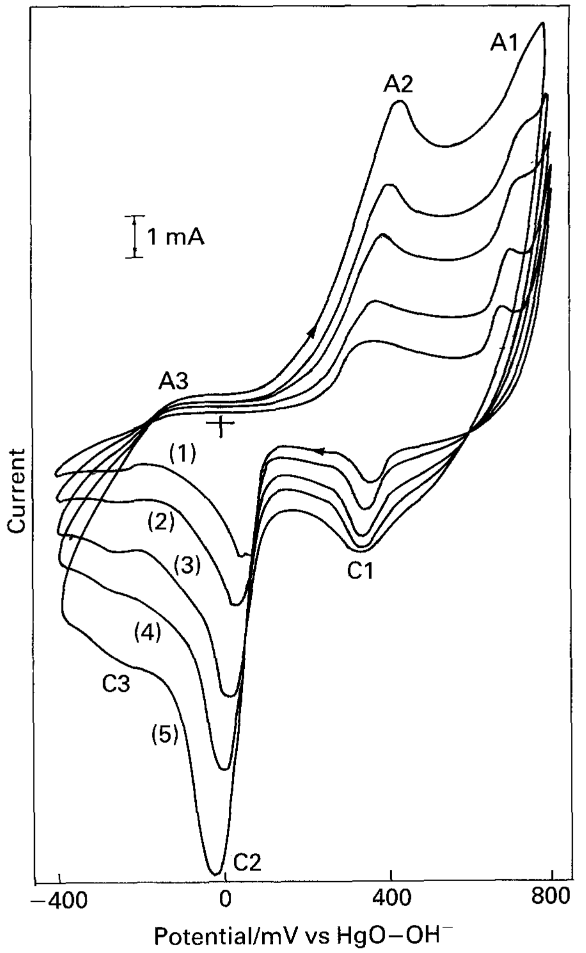

Fig. 1. Potentiodynamic profile for the alloy recorded after 1 h of RTPS between −400 and 800 mV at (1) 50, (2) 100, (3) 200, (4) 300 and (5) 500 mV s^{-1}.

The electrolyte was deaerated by bubbling nitrogen for 30 min. The annealed working electrode was polished using emery papers of different grades and degreased with acetone, followed by rinsing with triply distilled water. The electrode was reformed by means of a repetitive triangular potential sweep (RTPS) for 1 h at 100 mV s^{-1} between −400 and +800 mV, between the hydrogen and oxygen evolution potentials, respectively. After RTPS, cyclic voltammograms were recorded between different ranges of potential and the impedance spectrum was also obtained.

The electrode surfaces before and after RTPS were examined using scanning electron microscopy (Jeol-JSM-35CF model) and X-ray diffraction analysis using a computer controlled powder X-ray diffraction system (Jeol-JDX-8030 model). Annealed and mechanically polished alloy specimens were kept in a high vacuum desiccator after preparation. The SEM and XRD examinations were carried out within 30 min. of specimen preparation. In this study, bare electrode refers to the annealed mechanically polished and unreformed alloy kept for 30 min. in deaerated 0.5 M NaOH solution.

3. Results and discussion

3.1. *Cyclic voltammetry*

Figure 1 illustrates potentiokinetic traces of the alloy in aqueous 0.5 M solution. The potential scan covered the range −400 to +800 mV on the anodic side and +800 to −400 mV on the cathodic side i.e. between the hydrogen and oxygen evolution potentials. Three anodic (A1, A2, A3) and three cathodic peaks (C1, C2, C3) are visible.

The electrode, after RTPS pretreatment was scanned at three different potential ranges i.e., −100 to +300 mV, −400 to +100 mV and +200 to +800 mV vs. Hg|HgO|OH$^-$ electrode and Fig. 2(a)–(c) shows cyclic polarization curves obtained in this way. The charge calculated from these CVs shows that the charge released in anodic processes (A1, A2, A3) seems to exceed significantly that consumed in the corresponding reduction peaks (C1, C2, C3).

Comparison of the resulting potentiodynamic *I–E* profiles with those obtained for the pure metals shows that the current in A3 is related to the oxidation of metallic copper to Cu(I), which undergoes further oxidation to Cu(II), i.e. peak A2. The oxidation of metallic silver to Ag(I) occurs at a potential corresponding to A1. C1 may be attributed to the reduction of silver and C2 and C3 correspond to the reduction of copper species [7, 10].

Figure 1 illustrates the effect of increasing sweep rate on the potentiokinetic behaviour of the alloy. The intensity of the anodic peak currents clearly increases. The cathodic peak potentials shift to more negative values, whereas the anodic peak potentials remain constant, indicating that the cathodic reduction is taking place on a porous passive film [11].

Fig. 3 indicates the dependence of i_p on $\nu^{1/2}$ (ν being the scan rate) for anodic potentials at −100, +390 and

Table 1. X-ray diffractogram data

Peaks	*Bare electrode*		*Treated electrode*	
	2θ/degrees	*d/nm*	*2θ/degrees*	*d/nm*
1	13.500	0.6553	13.700	0.6458
2	16.400	0.5401	16.500	0.5368
3	18.000	0.4924	18.200	0.5870
4	20.600	0.4308	20.800	0.4267
5	38.600	0.2331	38.200	0.2354
6.	44.100	0.2058	43.806	0.2065
7	65.000	0.1434	64.700	0.1440
8	77.300	0.1233	77.400	0.1232

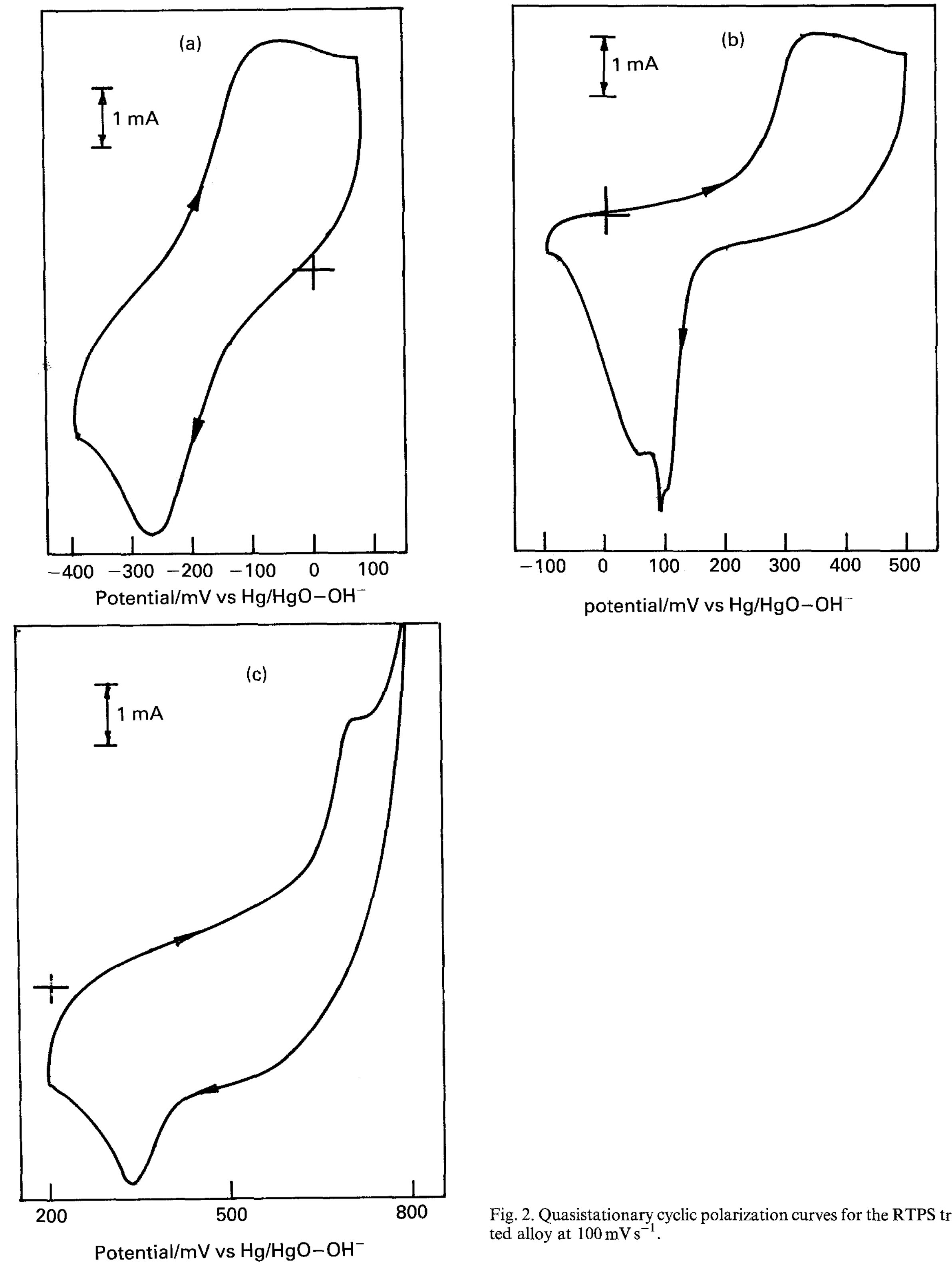

Fig. 2. Quasistationary cyclic polarization curves for the RTPS treated alloy at 100 mV s^{-1}.

+700 mV (Fig. 1). A linear dependence is observed in all the cases. However, the slope value is different for different peaks, thus indicating that the anodic film formation does not follow the same mechanism. Cyclic voltammograms are reproducible, even after fifteen days of RTPS.

3.2. *Impedance measurements*

Impedance measurements were performed in the frequency range 100 mHz to 10 kHz to characterise the surface at three potentials after RTPS, which corresponds to $E_{1/2}$ of three peaks obtained for cyclic polarization curves shown in Fig. 2(a)–(c). The impedance spectrum is almost a vertical line showing that the interfacial impedance was purely capacitive due to the presence of a passive film on the surface [12, 13].

3.3. *Surface analysis*

The SEM analysis of the electrode surface depicted the pronounced effect of the RTPS experiments, as

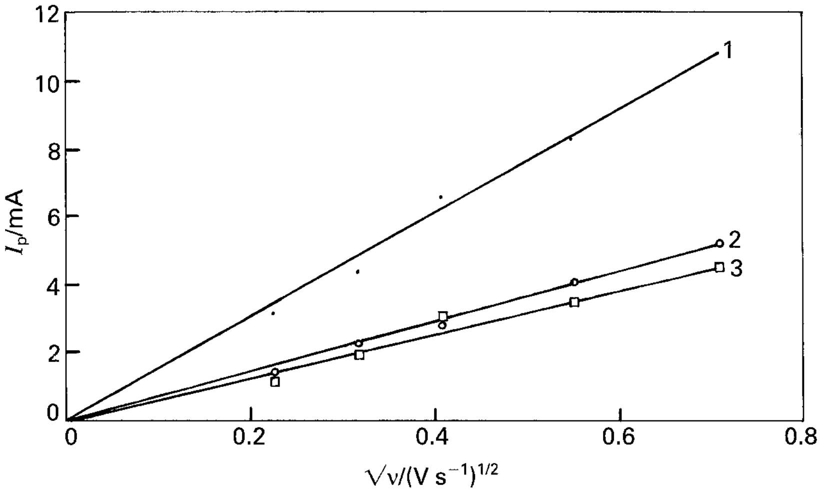

Fig. 3. I_p vs. $\nu^{1/2}$ plot for the anodic peak potentials: (1) −100, (2) 390 and (3) 700 mV.

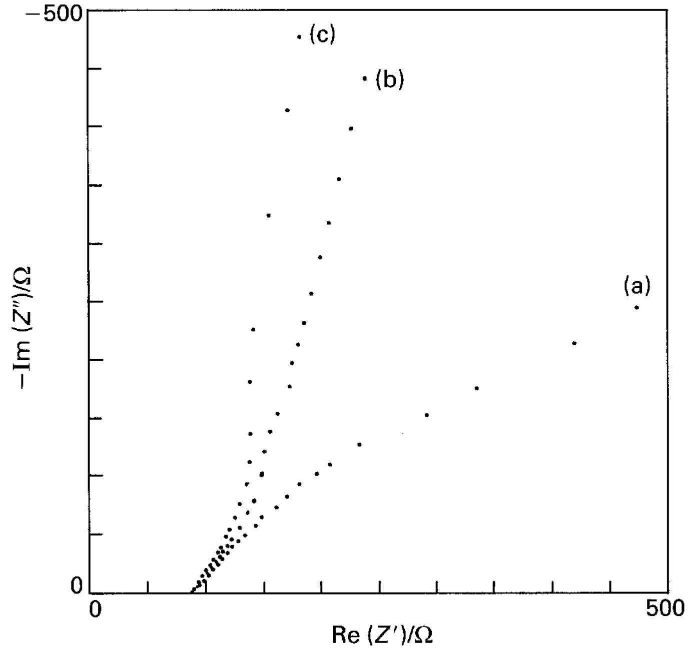

Fig. 4. Impedance spectrum for treated electrode at different potentials: (1) −175, (2) 225 and (3) 550 mV.

shown in Fig. 5(a) and (b). The bare electrode micrograph in (a) shows only a featureless structure, whereas (b) shows the relatively uniform surface covered with a thin precipitate and there were spots of localized corrosion in the deposit [14]. The surface can be divided into three different regions, the grain boundaries being well defined, having white and dark grains. The dark grains may be due to the preferential dissolution of aluminium from the surface and white grains may be due to the deposition or the presence of oxidized products of Ag and Cu.

X-ray diffraction patterns obtained for electrodes before and after RTPS experiments are shown in Fig. 6(a) and (b). The electrode before treatment (bare electrode) has a crystalline nature, whereas after treatment it shows a slightly amorphous

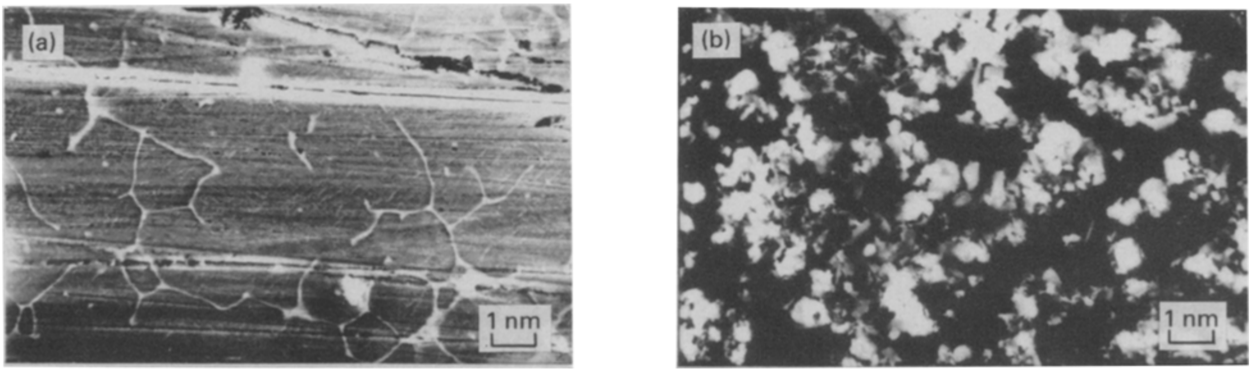

Fig. 5 (a) Scanning electron micrograph (a) for bare electrode [6442], and (b) for treated electrode [6441] (after RTPS pretreatment the electrode was removed at +800 mV).

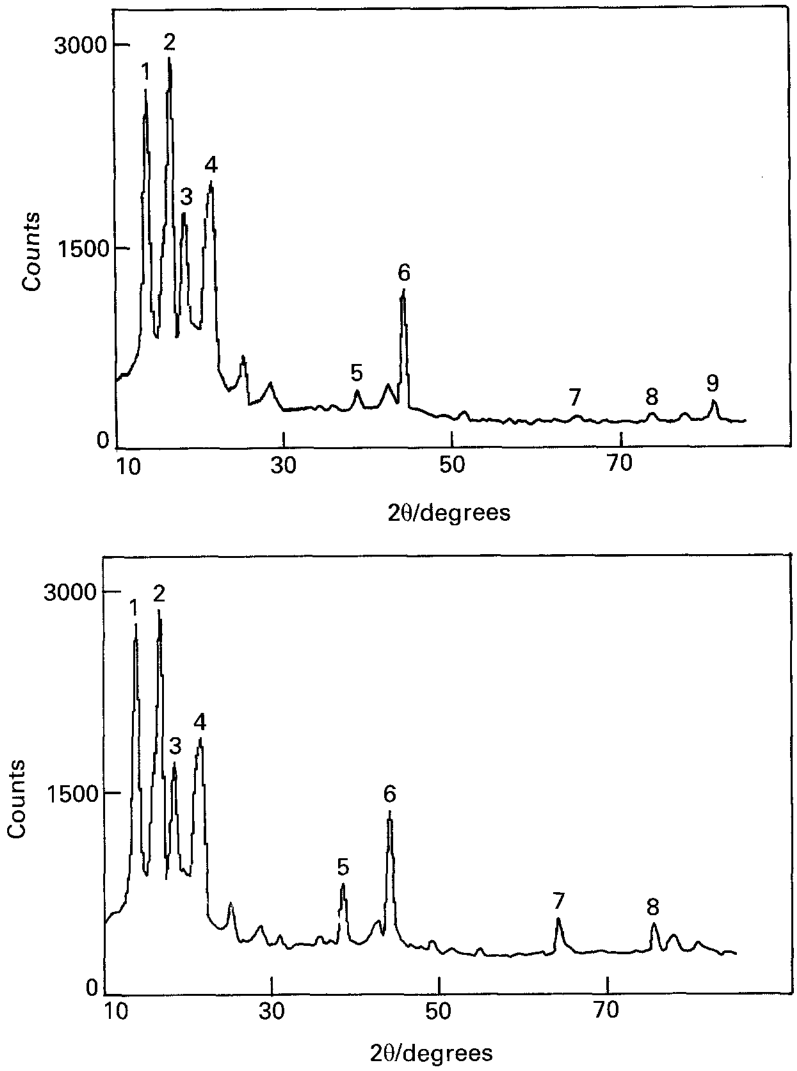

Fig. 6 (a) X-ray diffraction spectrum (a) for bare electrode, and (b) for treated electrode (after RTPS pretreatment the electrode was removed at +800 mV).

nature, revealing a small decrease in *d* values and increase in 2θ values (Table 1) [11]. Such behaviour is due to the formation of oxides on the surface.

4. Conclusion

The potentiokinetic polarization of the alloy (Cu–Al(19%)–Ag(19%)) in sodium hydroxide solution leads to the formation of a nonuniform passive film and elimination of aluminium on the surface. It also facilitates the deposition of copper and silver on the surface. The impedance study indicates the formation of a thin oxide layer film; this is also confirmed by SEM and XRD studies. The material used has properties similar to those reported earlier for low aluminium alloys.

Acknowledgements

The authors thank the Director of CECRI for the facilities to carry out these experiments. One of the authors (MAN) thanks CSIR (India), for the award of Senior Research Fellowship.

References

[1] D. Stoeckel, *Adv. Mat. Pro,* **10** (1990) 33.
[2] C. Panseri and M. Leoni, *Allumino.* **30** (1961) 289.
[3] R. Z. Nakazato, A. C. Guastaldi, A. V. Benedetti and M. Cilense, Proceedings of the 12th SENACOR conference, Brazil (1985) p.62.
[4] T. B. Mazzalski and J. H. Perepezke, *Z. Metallkde* **64** (1973) 176.
[5] A. T. Adorno, M. Cilense and W. Garlipp, *J. Mater. Sci. Lett.* **6** (1987) 163.
[6] *Idem, ibid.* **8** (1989) 281.
[7] R. Z. Nakazato, P. T. A. Sumodjo and A. V. Benedetti, *Electrochim. Acta* **5** (1987) 263.
[8] P. L. Cabot, F. A. Centellas, J. A. Garrido, P. T. A. Sumodjo, A. V. Benedetti and R. Z. Nakazato, *J. Appl. Electrochem.* **21** (1991) 446.
[9] A. V. Benedetti, R. Z. Nakazato, P. T. A. Sumodjo, P. L. Cabot, F. A. Centellas and J. A. Garrido, *Electrochim. Acta* **36** (1991) 1409.
[10] N. A. Hampson, J. B. Lee and K. I, MacDonald, *J. Electroanal. Chem.* **32** (1971) 165.
[11] D. W. Shoesmith, J. E. Rummery, D. Owen and W. Lee, *J. Electrochem. Soc.* **123** (1976) 790.
[12] R. D. Armstrong and M. Henderson, *J. Electroanal. Chem.* **32** (1971) 1.
[13] *Idem, ibid.* **40** (1972) 121.
[14] M. Drogowska, L. Brossard and H. Menard, *J. Electrochem. Soc.* **13** (1992) 2787.