

Behaviour of lead-silver-tin alloy under the influence of A.C. superimposition

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The electrochemical behaviour of Pb-Ag (0.5%)–Sn (1.5%) alloy under the influence of superimposed a.c. has been investigated by galvanostatic polarisation technique. It has been observed that a.c. acts as a powerful depolariser and the effect is dependent on d.c. density as well as d.c.: a.c. ratio. Selective dissolution has been observed along the grain boundaries. The formation of PbO_2 has been increased by a.c. at higher d.c. densities whereas no significant effect is observed at low d.c. densities. The depolarisation is mainly due to pulsating field and also partly due to porous film formation and continuous dissolution of the substrate.

Key words: A.C. superimposition, lead alloy, passivation

INTRODUCTION

Anodic behaviour of lead alloys has been studied extensively and continuous search has been on for antimony free lead alloys as grid material. Alloys containing Sn as one of the components have been studied for this purpose [1–3]. During charging from a rectifier, there is always an a.c. ripple accompanying the d.c. and this ripple has been known to influence the polarisation behaviour of lead alloys [4]. The polarisation characteristics of Pb–Ag (0.5)–Sn (1.5) under the influence of an a.c. ripple superimposed over the electrolysing d.c. in 7.916N H_2SO_4 are reported in this paper.

EXPERIMENTAL

Investigations have been carried out under galvanostatic conditions covering a d.c. range from 1.0 to $10\text{mA}\cdot\text{cm}^{-2}$ with superimposing of a.c. of varying magnitudes from 0 to 100% of d.c. value. The details of the cell etc. are given elsewhere [4]. The process of polarisation was studied by open circuit discharge and also by reverse polarisation.

RESULTS AND DISCUSSION

The anode potential was measured with time during polarisation with and without a.c. superimposition and a typical E-t plots at d.c. $1\text{mA}\cdot\text{cm}^{-2}$ are given in Fig. 1. In addition to the Pb/PbSO₄ plateau at -0.90 to -0.95V there is a small step at -0.025 to $+0.056$. This second step occurs at low d.c. densities and is almost absent at D.C. $> 5.0\text{mA}\cdot\text{cm}^{-2}$. The a.c. has been found to reduce this

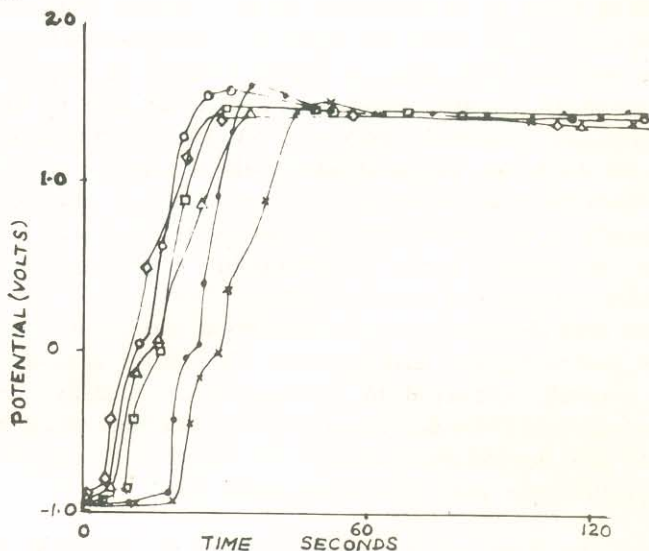


Fig. 1: Polarisation at $1.0\text{mA}\cdot\text{cm}^{-2}$ with A.C. superimposition
 ○—○ D.C. only ×—× 5% A.C. ●—● 10% A.C.
 △—△ 20% A.C. □—□ 50% A.C. ◇—◇ 100% A.C.

plateau considerably. The effect of a.c. on the Pb/PbSO₄ plateau is also dependent on d.c. density as well as on a.c. percentage. At low d.c. this is decreased with increase in a.c. whereas at higher d.c. the dissolution is increased as indicated by elongation of this step. The depolarising effect of a.c. is evident from the flattening of the passivation peak at high a.c. and also by lowering of the overpotential. This effect is more pronounced at high d.c. densities and high percentages of a.c. The Tafel slope was unaltered by low percentages of a.c. but considerable reduction was observed at high a.c. superimposition. Figure 2 shows the behaviour

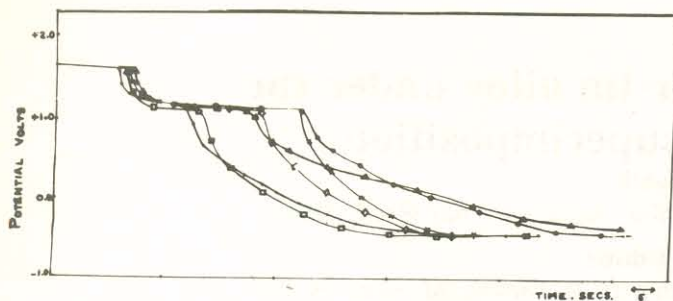


Fig. 2: Open circuit discharge after polarisation with A.C. superimposition

○—○ D.C. only ×—× 5% A.C. ●—● 10% A.C.
 △—△ 20% A.C. □—□ 50% A.C. ◇—◇ 100% A.C.

on open circuit discharge after polarisation at 1.0 mA.cm^{-2} d.c. for 5 mins. After an initial fall, the film of PbO_2 undergoes steady discharge at $+1.05$ to $+1.10\text{V}$ and the time taken to reach the break-off point at $+0.75$, which can be taken as an indication of the available PbO_2 , is decreased by a.c. After this point, on prolonged discharge the potential falls down to $-0.45 \pm 0.05\text{V}$ at which it remains for a considerable time and finally falls to the equilibrium potential $-0.95 \pm 0.05\text{V}$ after several hours of self discharge. The electrodes could be taken as having levelled off near $-0.45 \pm 0.05\text{V}$ and in these cases the porosity of the surface film is the controlling factor for the time taken to reach this level point. These have been additional points of arrest at -0.6 , -0.73 and -0.95 which have been identified by earlier workers as corresponding to the lead oxides and lead sulphate. Though the behaviour is generally unaltered by increase in d.c. density, the formation of PbO_2 is increased by a.c. superimposition of 5 to 20% beyond which there is no change as determined by coulometric reduction of the anodic film.

On the basis of the results presented above, it is evident that the a.c. acts as depolariser and this action is pronounced at high d.c. densities and also high percentages

of a.c. At low d.c. densities with low a.c. there is a selective dissolution of certain phases of the alloy as indicated by a potential step at -0.025 to $+0.056\text{V}$ in E-t curve. The alloy has been found to be a composite of the different binary eutectics between lead and Ag_3Sn and the selective dissolution of the Ag_3Sn phase which is more concentrated at the grain boundaries could have been accelerated by a.c. as was found on microscopic examination of the surface and also the film formed during polarisation. The possibility of such a dissolution has been confirmed by a corresponding peak in the potentiostatic investigations of the alloy. All these can be very well explained on the basis of the fact that d.c. with superimposed a.c. is nothing but a pulsating d.c. with maxima and minima corresponding to those of the a.c. At high a.c. values there is a cathodic portion of the current and the pulsating d.c. is converted to asymmetric a.c. ($\text{a.c.} > \text{d.c.}/\sqrt{2}$) and the completing reaction of H^+ discharge may take place along with the anodic reaction. The relative proportions in which the two reactions occur depend on the d.c. as well as a.c. densities and their relative ratios. This has led to powerful depolarisation of the anode. Increased porosity of the film due to selective dissolution as well as disrupted film formation also contributes to the depassivation phenomenon. On a comparison with the binary alloys of Pb.Ag and Pb.Sn the behaviour of ternary alloy has been found to show a better promise towards improved corrosion resistance even under a.c. superimposition.

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