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Effect of Water and Chloride Ions on the Polarisation Behaviour of 1060 Aluminium in Nitrobenzene and Aniline

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Effect of water and chloride ions on the polarisation behaviour of 1060 aluminium in nitrobenzene and aniline has been studied using potentiostatic method. Anodic S-shaped curve has been obtained only in nitrobenzene. A shift towards lower current density in the polarisation curve has also been noticed in nitrobenzene having water and chloride ions. Addition of water in aniline bodily shifts the curves towards the higher current density. An interesting cathodic polarisation curve () has been found in the case of nitrobenzene.

INTRODUCTION

Inhibitive tendency of organic compounds containing 'N' atom has been reported for aluminium in different media[1-4]. Extensive literature survey has revealed that very little attempt has been made to study the effect of such compounds on the metal surface in the absence of corrosive media.

The aim of this paper is to elucidate the mechanism of the effect of nitrobenzene and aniline on the 1060 aluminium by potentiostatic method.

EXPERIMENTAL

All the chemicals were of AnalaR grade. 1060 aluminium having following composition was supplied by Hindalco, Renukoot, Mirzapur: Si = 0.12%, Fe = 0.02%, Mn = 0.04% and Al = 99.82%.

All the experiments were carried out using a Wenking L.B. 75 (M) laboratory model potentiostat. The area of the electrodes used was 10 × 10 mm. The shape of the electrode was just like a flag. The preparation of electrodes and the method of cleaning were the same as described earlier[2]. After the determination of steady state corrosion potential of the electrodes, cathodic and anodic polarisation studies were carried out at 35°C in the same way as reported by Yadav *et al.*[1]

RESULTS AND DISCUSSION

The steady state corrosion potentials for 1060 aluminium in pure compounds

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undertaken for investigation as well as in the presence of water and chloride ions are given in Table 1. It is seen from this table that the steady state corrosion potential in aniline for aluminium has shifted towards active direction on adding 5 ml/L water in aniline. Further addition of water to aniline shifts the steady state corrosion potential in noble direction (less negative). The same trend of shifting in the potential is also noticed if 100 ppm KCl is added. Nitrobenzene has registered the same shifting trend of potential with an exception that 100 ppm KCl addant in this case reverses the direction of the change.

TABLE 1
STEADY STATE CORROSION POTENTIAL FOR 1060 ALUMINIUM IN THE ABSENCE AND IN THE PRESENCE OF ADDITIVES AT 35°C

Solution composition	Steady state corrosion potential (mV)
Nitrobenzene	–894
Nitrobenzene + 5 ml/L water	–810
Nitrobenzene + 5 ml/L water + 100 ppm KCl	–813
Aniline	–813
Aniline + 5 ml/L water	–838
Aniline + 15 ml/L water	–805
Aniline + 30 ml/L water	–780
Aniline + 30 ml/L water + 100 ppm KCl	–748

Anodic polarisation measurements were carried out in pure nitrobenzene and aniline, in presence of different amount of water and 100 ppm KCl. The results are shown in Figs. 1 and 2. It is evident from Fig. 1 that the active-passive nature is exhibited by 1060 aluminium. This nature of the curve does not change either on adding water or 100 ppm KCl. It is further seen that the fall in the current density in the passive region in presence of additives is larger as compared to their absence. It is obvious from Fig. 2 that the polarisation curves are shifted towards higher current density region with increase of water. But 100 ppm KCl is responsible for shifting the curves in lower current density region.

The cathodic polarisation results are shown in Fig. 3 for nitrobenzene. It is seen from figures that the curves in the presence of additives are less polarised than the curves in their absence. Aniline shows similar behaviour of cathodic polarisation. A peculiar type of curve () is found in pure nitrobenzene. The reason for this behaviour is still unknown.

The results can be explained on the basis of some physical organic principles *viz.* electron density at benzene nucleus, availability of an atom rich in electron in the substitutent group, presence of substitutent groups with +I, –I and other effects. The passivation behaviour of the metals in the electrolytes is due to formation of an additional interface between electrolyte and metallic surface. This interface is either of the corrosion products or of the oxide film. In nitrobenzene the inductive and resonance effect act in the same direction resulting in the decrease of electron density at the ring of it. Due to this nitrobenzene rich in electrons at oxygen will interact with anodic sites of aluminium and form a film

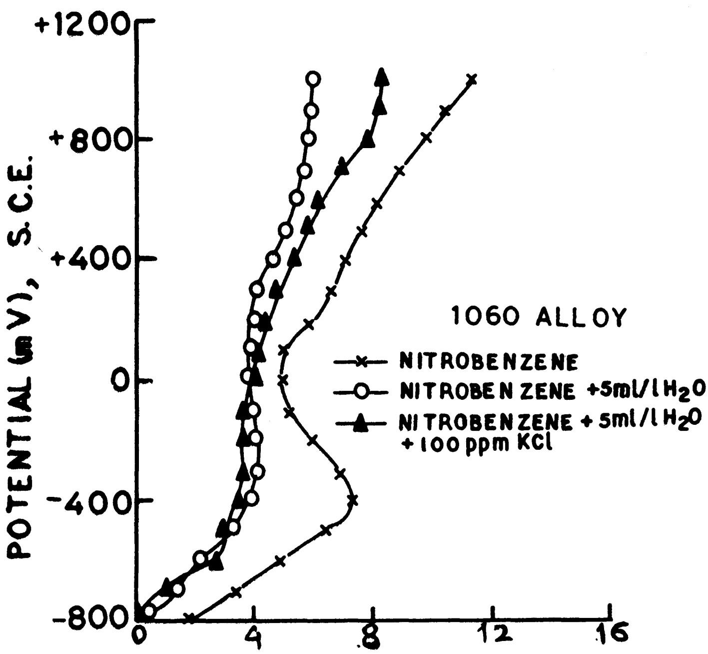

Fig. 1 Anodic polarisation curves for 1060 aluminium in nitrobenzene

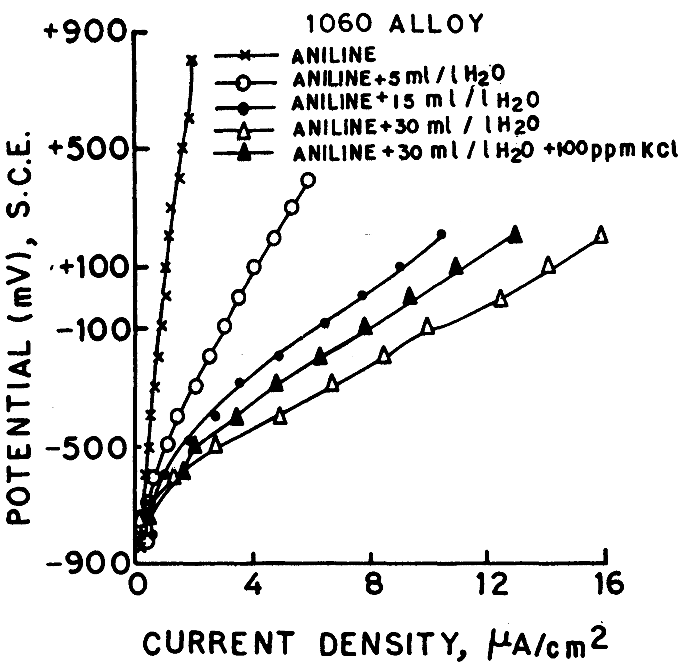

Fig. 2 Anodic polarisation curves for 1060 aluminium in aniline

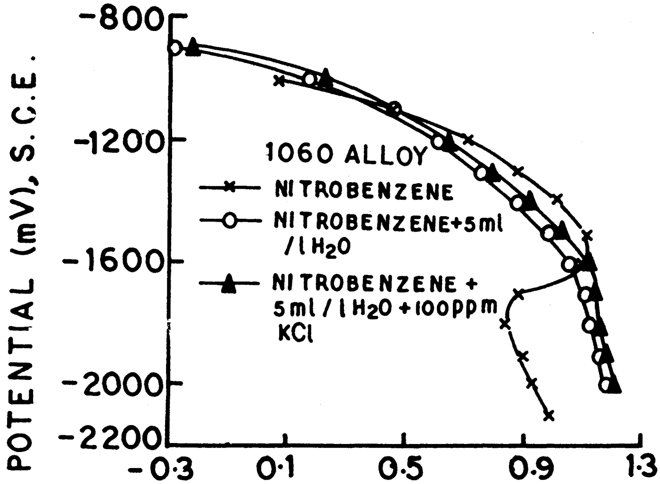

Fig. 3 Cathodic polarisation of 1060 aluminium in nitrobenzene

on its surface. This formed film increases the resistance, therefore, current density decreases in the anodic polarisation with increase in potentials. $-NH_2$ Group of aniline is electron pumping group. This group increases the electron density of benzene nucleus by acquiring +ve charge on nitrogen atom due to resonance. This indicates that aniline does not interact with anodic part of the metal surface. Hence aluminium does not exhibit active-passive behaviour in aniline.

When water is added to nitrobenzene the anodic polarisation curve moves towards lower current density region. Both nitrobenzene and water are polar in nature. They may link to one another. Therefore, it may be suggested that nitrobenzene interacts with anodic points of the aluminium along with water molecules and covers large surface area. Hence this is a responsible factor for the shifting of the curves towards lower region. The aggressive anion, Cl^-, forms a bridge between metal and nitrobenzene. This explanation is also supported by the fact that the breaking of the film starts at lower potential in the presence of Cl^- ion.

Aniline forms anilinium ion ($Ph\text{-}\overset{+}{N}H_3$) with water as follows:

$$Ph\text{-}NH_2 + HOH \rightleftarrows Ph\text{-}\overset{+}{N}H_3 + OH^-$$

It is clear that there is no possibility of the interaction of the anilinium ion with anodic sites of the metal. This may be a cause to move the anodic curves towards higher region in aniline having water.

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