Anodic Polarization of Chromium-Nickel Amalgam in Acidic Solutions

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The polarization curves obtained at chromium-nickel amalgam electrode in 0.1, 1.0 and 3.0 N H_2SO_4 solutions at 25° C. under constant currents exhibited several steps corresponding to the formation of mercurous sulphate, NiO/Ni_3O_4, $HCrO_4^-$ and oxygen evolution. The relation between the polarizing current and the time of passivation shows the coulombic nature of passivation.

The anodic behaviour of nickel in sulfuric acid solutions has received widespread attention by numerous investigators [1-7]; the anodic behaviour of chromium in sulfuric acid also has been studied, though less thoroughly [4-8]. However, relatively little data are available on the anodic behaviour of binary amalgam alloys of Cr-Ni in H_2SO_4 solutions.

The presence of trace amounts of base metal in the form of amalgam alters the anodic polarization chracteristics of pure mercury. Such impurities reflect themselves in the form of potential transient characteristic of the base metal. The study of the anodic behaviour of metallic amalgams offers some advantages over that of solid metal electrodes of which three deserve mentioning.

i) It allows a new variable, viz., the metal atom concentration, to be examined. This helps in gaining a deeper insight into the mechanism of passivation of metal.

ii) Amalgams can be easily prepared in a high state of purity and thus the effect of other metallic impurities (common in solid metals) is excluded.

iii) Due to the liquid nature of the amalgam, both the geometrical and the true surface area of the electrode are the same and hence current density values are more true and not just nominal.

The present investigation deals with the study of the galvanostatic polarization behaviour of composite amalgam (chromium - nickel) electrode in acidic solutions, with the aim of understanding the conditions leading to film formation and passivation on the surface of the metal and the role of the metal atoms therein.

EXPERIMENTAL

Composite Cr-Ni amalgam of definite metal atom contents were prepared by electrodeposition from acid solutions [9]. Complete deposition of the metal was ascertained by atomic absorption analysis and by EDTA titration. The amalgams were washed several times with distilled water and then dried by small strips of filter paper.

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The electrical circuit used in tracing galvanostatic polarisation curves of the amalgam electrode was previously described [10]. A high impedance digital voltmeter was used for accurate measurements of the anode potential. All experiments were conducted at 25±1°C. Each experiment was carried out using a fresh quantity of test solutions (0.1, 1.0 and 3.0 N H_2SO_4). The area of the amalgam electrode was 2.30 cm^2.

RESULTS AND DISCUSSION

General Behaviour of Polarisation Curves

Galvanostatic anodic polarisation curves for composite Cr-Ni amalgams (0.392 x 10^{-1} wt % Cr and 3.19 x 10^{-1} Wt. % Ni) in H_2SO_4 solution of various concentrations are given in Fig. 1 (A, B, C). The polarization curves are characterized by three steps:

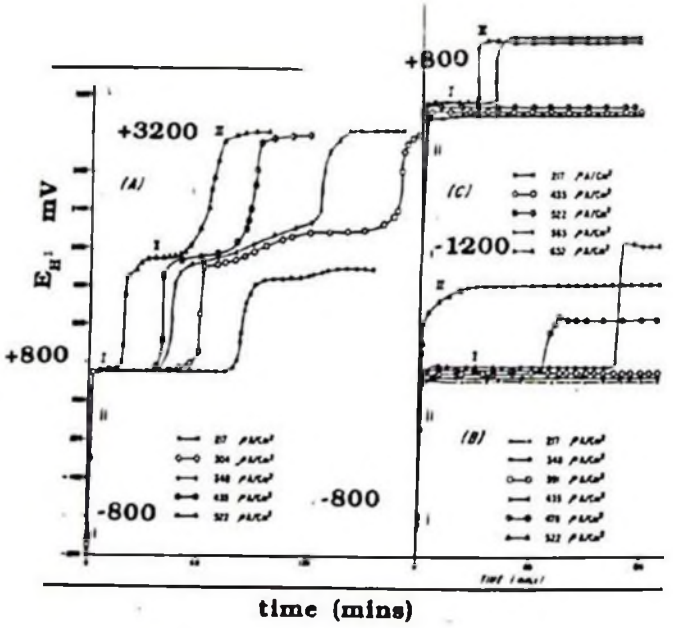


Fig.1 Anodic polarization of the composite amalgam 0.392 x 10^{-1} wt. % Cr + 3.19 x 10^{-1} Ni amalgam in
(A) 0.1 N. (B) 1.0 N and (C) 3.0 N H_2SO_4 at different current densities.

(a) The discharge region occurring at the very negative potential range of -1200 to -800 mV. This corresponds to discharging of the anodic double layer.

(b) A more or less elongated arrest (I) occurring at a potential of +650 to +700 mV, corresponding to the oxidation of mercury and nickel.

(c) A potential arrest (II) corresponds to oxidation of Ni and also dissolving $Cr(OH)_3$ as $HCrO_4^-$ ions (+1700 to +2000 mV).

(d) A potential arrest (III) at the very positive potential in the range +1250 to 3600 mV refers to oxygen evolution.

Upon anodic polarization, the initial negative potential changes instantaneously towards less negative values. The change is due to charging of the anodic double layer (region I). The potential range over which this process occurs, depends primarily on the magnitude of the polarizing current and to a lesser extent on the concentration of the electrolyte. Chromium amalgams were partly oxidized to Cr^{+++} and passed into solution [11] and partly remained as black powder on the surface of the amalgam. This led to the conclusion that along region II of the anodic polarization curve, the chromium of the amalgam is oxidized to chromic ions which hydrolyse to $Cr(OH)_3$.

Owing to the liquid nature of the electrode and decrease in the chromium content in the amalgam by the excessive dissolution of Cr from the amalgam (the formation of

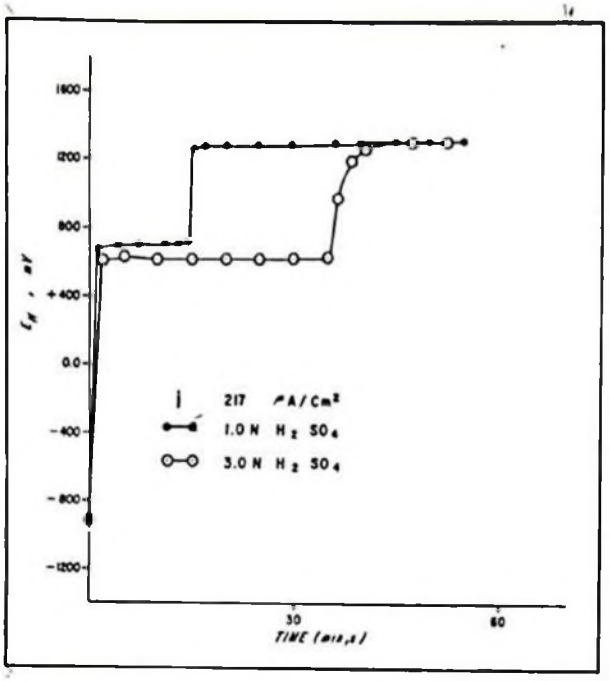


Fig. 2 Anodic polarization of Hg in 1.0 and 3.0 N H_2SO_4.

Cr^{+++} powder on the surface of the amalgam), the mercury of the electrode gets a chance to be oxidized; the potential rises to + 600 to + 750 mV (Fig.1 A-C) giving a clear step (I). The electrode surface becomes covered with white, green becoming yellow and black deposit. The same step is seen when pure mercury is polarised in the place of amalgam in the same electrolyte and same current density (Fig 2). So it is obvious that mercury is oxidised in this potential range to give mercurous sulphate. When Ni is present in the amalgam, this also is oxidised in the same potential region to give green to black nickel oxide. When the Cr- Ni amalgam electrode is polarized anodically in sulfuric acid solutions, Ni dissolves into the solution in accordance with reaction [14]

$$Ni + H_2O \rightleftharpoons NiO + 2H^+ + 2e$$

$$3\ NiO + H_2O \rightleftharpoons Ni_3O_4 + 2H^+ + 2e$$

The passive oxide film, is the duplex oxide of NiO and Ni_3O_4.

After this step, the potential rises again to give a clear step (II) at + 1800 to +2000 mV. This step II is marked in 0.1 N solution of H_2SO_4 (Fig. 1A), but this step is absent at higher concentration of H_2SO_4 (Fig. 1B,C), . The increase in potential along step II is accompained by an orange colour on the surface of the amalgam and is due to the second period of activity of the electrode corresponding to the dissolution of the chromic hydroxide formed earlier to $HCrO_4^-$ ions in the potential range of +1800 to 2000 mV. For the chromate process Oliver [15] gives

$$Cr^{+++} + 4\ H_2O \longrightarrow HCrO_4^- + 7H^+ + 3e$$

This process is followed by an increase in potential reaching the final step III. This represents oxygen evolution.

Polarizing Current - Passivation Time Curve

A plot of the logarithm of the passivation time against the passivating current for the same composite Cr - Ni amalgam were established in 0.1, 1 and 3.0 N H_2SO_4 acid solutions and gave a straight line whose slope is = 1 (Fig. 3). These results suggest a relation between the polarizing current "I" and the time of passivation " τ " for composite Cr - Ni amalgam electrode in H_2SO_4 solutions of the type $I\tau$ = constant, thus the mechanism of passivation of composite Cr-Ni amalgam in H_2SO_4 can be considered as being coulombic in nature. In this respect, the mechanism of passivation of composite amalgam is similar to the Cr amalgam in oxalic and

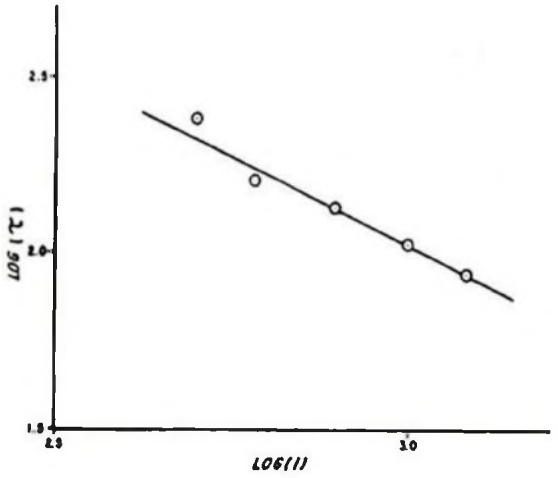


Fig. 3 log i - log τ relation for the composite amalgam 0.392 x 10^{-1} wt. % Cr + 3.19 x 10^{-1} wt. % Ni in 0.1 N H_2SO_4.

phosphoric acid and differ in nature in case of Ni amalgam in H_2SO_4 [16] where the mechanism of passivation was governed by the rate of metal diffusion to the electrode surface. This result indicates that in presence of chromium, the process of oxidation of the nickel amalgam changes gradually from a diffusion controlled to a coulombic process. A possible explanation for this effect may be arrived at if one imagines that, when the Cr atoms are regenerated by the displacement reactions, they do not stick to the electrode surface but are transfered to the oxide phase as such. The presence of Cr atom in the NiO lattice may alter its type of conductance from an ionic to an electronic mechanism. This can be achieved by the Cr atom contributing its free electrons and thus introducing electronic conductance. Hence the slope of the log i - log τ plot changes from -0.2 (characteristic of ionic conducting oxides) to -1 (characteristic of electronic conducting films).

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