EFFECT OF IODIDE IONS ON POLYCRYSTALLINE BRASS

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Cuprous iodide precipitates and crystallises in the form of triangular pyramids, and dendrites grow when brass (60% Cu and 40% Zn) is immersed in aerated acid copper sulphate solution containing HI. In the deaerated solution there is no precipitation of cuprous iodide even at appreciable concentration of HI.

It has been shown that iodide ions present in an electrolytic bath modify the habit of copper electrodeposited on the (100), (110) and (111) face of copper[1-3]. Triangular pyramids and dendrites grow when copper was deposited at 2 mA/cm² from an acid $CuSO_4$ bath containing HI at high concentrations of iodide ions. According to Piontelli[4] the effect of anions depends on the molecular polarisation and their size. The anions are strongly corrosive when they are present in large amounts in electrolytic baths and favour coarse crystalline dendritic powdery deposits.

The purpose of the present work is to investigate the effect of iodide ions on the polycrystalline brass of composition (60% Cu and 40% Zn) in aerated and deaerated solutions.

EXPERIMENTAL

A cylindrical brass rod (10 mm diamater × 10 mm length) was introduced into a plastic tube so that only the desired surface was exposed. This surface was mechanically polished on 3/0 and 4/0 emery paper and electropolished in (1 : 1) H_3PO_4. Pure Nitrogen was bubbled through purified solution of 0.25M $CuSo_4$ + 0.1M H_2SO_4 containing various amounts of HI for one hour just before each experiment. The specimen was immersed in the solutions (aerated or deaerated) for 30 minutes. The dried surface after washing with conductivity water and ethyl alcohol was examined under a metallurgical microscope. The solutions were prepared using conductivity water and pre-electrolysed.

RESULTS

Electropolished polycrystalline brass becomes etched when immersed in aerated solution containing HI up to a concentration of 1×10^{-6}M. At 1.5×10^{-6}M, dark specks of cuprous iodide in the background of etched surface were noticed (Fig. 1). When the concentration of hydroiodic acid is increased to 1.75×10^{-6}M of HI, some triangular pyramids were observed in the background of etched surface (Fig. 2). Dendrites of Cu_2I_2 begins to grow in large numbers when the concentration of HI is increased to 2×10^{-6}M of HI (Fig. 3).



(1) (2) (3)

Fig. 1: Dark specks of cuprous iodide in the Background of etched surface at 1.5×10^{-6}M HI on brass (×625)

Fig. 2: Triangular pyramids in the background of etched surface at 1.75×10^{-6}M HI on brass (×625).

Fig. 3: Dendritic growth with triangular pyramids with 2×10^{-6}M HI on brass (×625).

Further the duration of immersion of the surface for growth of cuprous iodide decreases with increase of concentration of HI. There was no precipitation of cuprous iodide on polycrystalline brass when it was immersed in deaerated solution containing 5×10^{-6}M of HI, but the surface became etched.

DISCUSSION

When electropolished surface of polycrystalline brass is immersed, copper preferentially dissolves in the solution. While dissolving in aerated solution, the Cu^+ ions may accumulate in the diffusion layer at the interface. As the accumulation of Cu^+ ions reaches a critical value, exceeding the solubility of 2.2×10^{-6}M there is precipitation of cuprous iodide in the form of triangular pyramids and dendrites[6]. It is known that cuprous iodide precipitates in the form of triangular pyramidal crystals having isometric tetrahedral symmetry ($\bar{4}3M$).

The precipitation occurs first in the aerated solution only, even though Cu^+ ions are formed at the surface in deaerated solution by the following reaction:

$$Cu^{++} + Cu \rightleftharpoons 2Cu^+$$

The above reaction is too slow and may not provide enough Cu^+ ions to exceed the solubility of cuprous

iodide in conformity with the observation of Bockris and Mattson[8]. The dissolved oxygen favours the formation of Cu^+ ions by the reaction

$$O_2 + 4Cu + 2H^+ \rightarrow 4Cu^+ + 2\,OH^-$$

and thereby provides enough Cu^+ ions for the precipitation of cuprous iodide. Hence it could be concluded that the presence of oxygen is necessary for the precipitation of cuprous iodide.

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