

ELECTROPLATING OF IRON-PHOSPHOROUS ALLOY PART I-INFLUENCE OF REDUCING AGENTS ON THE STABILITY OF THE PLATING BATH

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This paper examines the reactions that take place in an iron plating bath during the plating of iron on copper. The influence of adding reducing agents viz., iron powder, hydroxylamine, and hydrazine sulphate, on the bath performance is discussed.

Keywords: Iron-phosphorous alloy plating, reducing agents, bath stability.

INTRODUCTION

There is renewed interest in the electroplating of iron particularly on copper for the development of soldering tips. Unlike the plating of other metals, iron - plating is accompanied by certain chemical and physical changes in the bath resulting from autoxidation and initiation of coagulation. These changes pose challenges in the electroplating of iron. In the present paper the authors examine the factors responsible for the change in the characteristics of the iron plating bath and discuss the influence of reducing agents such as iron powder, hydroxylamine, and hydrazine sulphate on the serviceability of the bath.

EXPERIMENTAL

All the chemicals used were of Qualigen Extra Pure grade and the solutions were prepared using double - distilled water. IR spectra were recorded on a Shimadzu IR 408 spectrophotometer using KBr pellets. Thermogravimetric measurement was made using a Delta Series TGA 7 instrument. EPR measurements were made on a E4 Varian x band spectrometer.

RESULTS AND DISCUSSION

The composition of the iron plating bath is as follows.

iron as ferrous ammonium sulphate 200 g.l⁻¹

sodium chloride	40 g.l ⁻¹
formic acid	45 g.l ⁻¹
phosphorous acid	2 g.l ⁻¹
ammonium sulphate	70 g.l ⁻¹

The standard electrode potential $E(O_2/H_2O)$ of oxygen is 1.23 V [1], which can oxidise ferrous sulphate to basic ferric sulphate in air but the reaction (Eq. 1) is very slow, particularly more so in acidic values.



However, when the bath is put to use for iron plating, certain changes are noticed.

- (i) Current efficiency decreases upon continuous usage.
- (ii) Turbidity sets in although at a slow rate.
- (iii) Permanganimetric method of estimating Fe^{2+} and Fe^{3+} in the bath gives erratic results.

One may readily surmise that the reaction proposed in Eq. 1 was accelerated under plating conditions and was responsible for the changes. If such a proposition was true, then a way to retard the reaction was to add reducing agents to the bath.

In order to verify the proposition, the each of the following reducing agents was as an additive employed to the iron plating bath.

- (i) iron powder

(ii) hydroxylamine

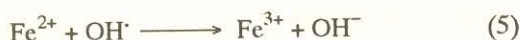
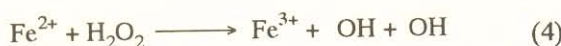
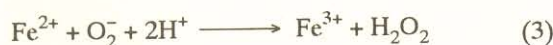
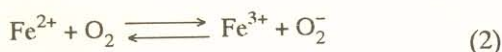
(iii) hydrazine sulphate

The influence produced by each of the reducing agents is presented below.

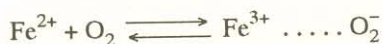
Effect of iron powder

Iron powder has been added to the bath with a view to reduce the Fe^{3+} ions back to Fe^{2+} . But we found that turbidity was more severe in the presence of iron powder than in its absence. In other words iron powder is found to catalyze the formation of Fe^{3+} rather than to reduce it.

Autoxidation of ferrous iron, proceeds by the following mechanism [2]:

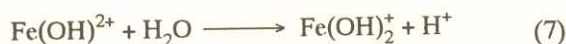
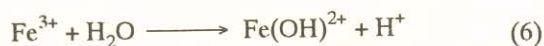


more precisely step (1) can be represented as follows.



This means that the reverse process leading to the restitution of ferrous ions and O_2 will be inhibited in the presence of anions/ligands that complex with Fe^{3+} . F^- and $\text{P}_2\text{O}_7^{4-}$ are known for complexing with Fe^{3+} and when these were added to the bath, a swifter turbidity was observed in the bath [3]. On the other hand, when the acetate ions are added the turbidity was not accelerated.

Upon aging (5 days) an iron powder added iron plating bath formed a flocculant precipitate. Hydroxylation is a common feature of the iron (III) system [3].



The hydrogen ions thus produced, can meet a part of the need for oxidation ($\text{Fe} \rightarrow \text{Fe}^{2+}$ or $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ (Eqn. 3)) and the iron-hydroxyl complexes will polymerize to polymeric ferric species. Polyferric sulphate (PFS) of the general formula $\text{Fe}_2(\text{OH})_n(\text{SO}_4)_{3-n/2}$ is a well characterised

inorganic coagulant and can be produced by the reaction of oxygen with acidic $\text{H}_2\text{SO}_4/\text{FeSO}_4$ solutions [4].

Such a compound can be readily identified by characteristic OH^- and SO_4^{2-} frequencies in the IR spectrum. Therefore, the precipitate was isolated from the bath, dried at 80°C in air and the IR spectrum was recorded. In the spectrum IR frequencies characteristic of organic moieties particularly of carbonyl/carboxylate functional groups were found. Where do the organic functionalities originate from? Formic acid is a constituent of the bath and could be the only source of organic functionality. In fact, the IR frequencies match with that of formate functional group (1700 cm^{-1} (s), 1600 cm^{-1} (s) and 1400 cm^{-1} (s) [5]. It is reasonable to presume that iron(III) formate is formed in the bath because iron(II) formate is only slightly soluble in water and is resistant to air oxidation: whereas, iron(III) formate is soluble in water, its aqueous solutions are subject to hydrolysis which results in the formation of basic formates. Eventually precipitation of iron hydroxide occurs liberating formate [6]. There is another impact of this event. Iron oxide as a catalyst has been shown to decompose formic acid and the oxidation proceeds via the formation of iron formate [7]. Thus an

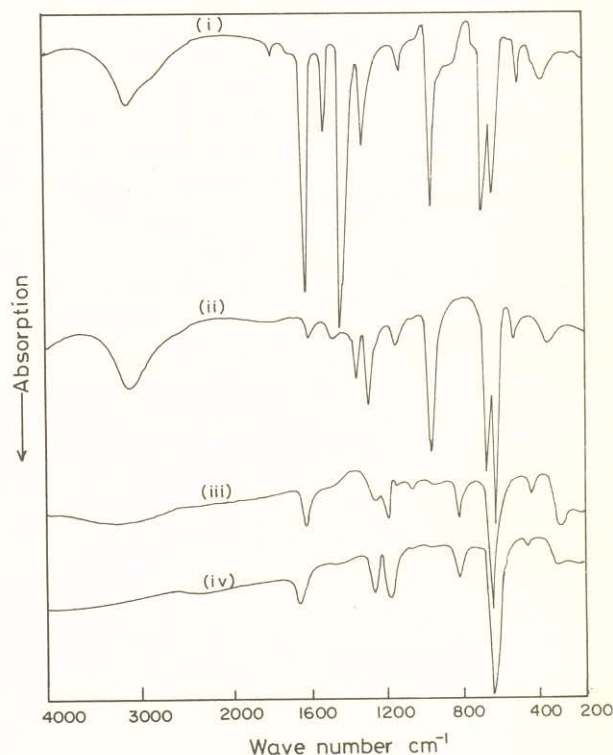


Fig. 1: IR spectra of the precipitate isolated from iron-powder added iron plating bath (i) fresh air-dried sample (ii) sample treated at 623 K (iii) sample treated at 1023 K (iv) IR spectrum of an aged precipitate after drying in air at 353 K for 6h

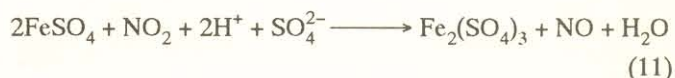
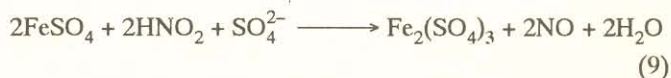
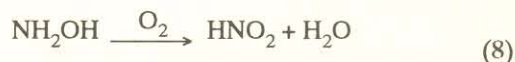
autocatalytic chain reaction sets in and destruction of the bath constituent results. When the precipitate isolated from the bath was treated at 623 K (5h) and the IR spectrum recorded, the frequencies characteristic of formate were absent and the spectrum exhibited the frequencies characteristic of OH (1000 cm^{-1} (s), 1750 cm^{-1} (s)) and sulphate ($1000\text{--}1150\text{ cm}^{-1}$ (s), $600\text{--}640\text{ cm}^{-1}$ (m) & 500 cm^{-1} (m) [8,9]). The broad absorption 3500 cm^{-1} is characteristic of bonded OH groups.

IR spectrum of the precipitate pretreated at 1073 K shows absorptions that could be associated only with sulphate and oxide groups. This observation support that the polymeric ferric sulphate has lost the OH groups during calcination and got converted into a mixed oxide - sulphate. Thermogravimetric analysis (Fig. 2) provides evidence to the aforesaid transformations.

Effect of hydroxylamine

Hydroxylamine, (NH_2OH) a well known reducing agent, does not exhibit reducing properties when added to an iron plating bath. When hydroxylamine is added to the bath, the solution turns yellow and then deep red. The red colour continues to persist while the solution starts to turn turbid. The turbidity is slow to begin with and is then very rapid. Eventually thick yellow flocculant precipitate separated from the solution. Analysis of the precipitate proved the presence of ferric and sulphate ions. This interesting observation can be explained on the basis of the possibility of formation of oxides of nitrogen from hydroxylamine. It is probable that hydroxylamine is first converted into nitrous acid by the action of the superoxide anion, O_2^- [10], the generation of the latter has now been proved. Nitrous acid could then be converted to nitric oxide, which brings about the oxidation of ferrous sulphate. Reports show that hydroxylamine can be oxidised by Cu(II) or Fe(II) [11,12]. Existence of at least some Cu^{2+} ions in the bath is not a remote possibility and

may arise as a result of a chemical reaction of the cathode in the absence of applied electric current. Thus a multitude of hydroxylamine oxidation modes are possibility in the bath. The major chemical reactions can be summarised as follows.



The oxidation rate of NO to NO_2 is very fast and it is NO_2 that oxidises the ferrous ions, regenerating nitric oxide to run the cycle until all the ferrous sulphate has been oxidised to ferric sulphate.

The authors observed a significant increase in the pH of the bath in the presence of hydroxylamine (Table I). This is because depletion of H^+ ions accompanies the formation of $\text{Fe}_2(\text{SO}_4)_3$ and pH elevation intensifies the coagulation. Upon aging (10 days), the suspension turned brownish yellow. The precipitate removed from the plating bath was found to contain Fe_2O_3 besides ferric and sulphate ions.

The EPR spectrum of the hydroxylamine added iron plating bath is shown in Fig. 3. Curve a. The spectrum provides evidence to the generation of free radicals in the bath; for instance, iron - nitrosyl species as an intermediate. Therefore, Eqn. 10 may not be true representation of NO_2 formation; instead it may proceed via a free radical mechanism, catalyzed by iron. Curve b in Fig. 3 is the EPR spectrum of the red-brown precipitate isolated from an aged bath. The 'g' value indicative of a Fe(III) species.

At higher pH values a reaction of the following type could take place leading eventually to the oxide formation.

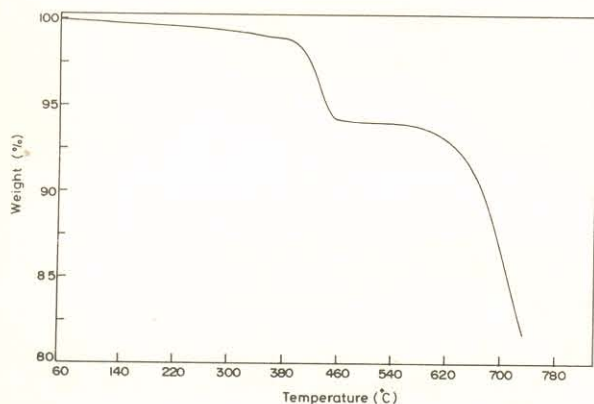
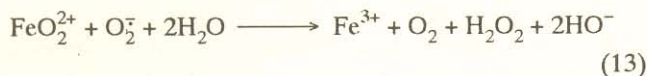


Fig. 2: TGA tracing of the precipitate separated from iron plating bath. The sample was pretreated at 353 K for 6h

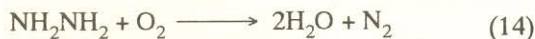
TABLE I: Relationship between the hydroxylamine content and the change in pH of the iron plating bath

Hydroxylamine content ($\text{mol} \cdot \text{l}^{-1}$)	pH
0	3.0
1×10^{-3}	3.8
1×10^{-2}	4.2
1×10^{-1}	4.7
1	5.3



Effect of hydrazine sulphate

Hydrazine is a reducing agent and an oxygen scavenger. It reacts with oxygen to give water and gaseous nitrogen although the reaction is slow.



The oxygen scavenging property of hydrazine has prompted its use for corrosion prevention of boilers [13], in electrochemical machining of chromium steel in NaNO_3 bath for extending the service life of the bath [14], in electroplating of smooth copper [15] and of lead alloys [16], treatment of annealed steel prior to electroplating [17] and to remove undesirable oxidizing contents in sulphuric acid [18].

Unlike hydroxylamine, the products of hydrazine oxidation are not expected to have any poisonous effect on the iron plating bath. Therefore hydrazine sulphate was employed as an additive to the iron plating bath. As expected, hydrazine sulfate (0.25 mol.l^{-1} to 0.8 mol.l^{-1} range) was quite effective in maintaining the stability of the bath but only in the absence of formic acid in the bath. In the presence of formic acid, emulsion formation and foaming were observed. This is owing to condensation of hydrazine and formic acid to form polymeric resinous matter [19].

Temperature increase has a pronounced influence on the stability of the hydrazine added iron bath during plating. This is because temperature increase accelerates the hydrazine decomposition enhancing its oxygen scavenging capacity. Best effects were observed at a temperature of $328\text{--}333 \text{ K}$ and at hydrazine content in the range 0.25 mol.l^{-1} to 0.8 mol.l^{-1} . It was also observed that by decreasing the pH of the medium to 1 to 2 hydrazine performed better and the quality of iron coating was superior. A similar observation has been made by Andreeva and Goldstein in the iron plating bath [20].

Another point of interest with hydrazine sulphate is the effect that it produces on the iron anodes. Iron anodes by virtue of inherent fast corrosion kinetics at the pH employed in the present study, dissolves much in excess to that expected from the applied current density [21]. In the presence of hydrazine sulphate, a reduction in the excessive dissolution of iron (by weight loss measurements) was noted. The controlling effect of hydrazine on the anodic process can be attributed to the adsorption at the anode of hydrazine and its intermediate dissociation product for instance diimine $\text{NH}=\text{NH}$ [22].

The authors noticed that an iron plating bath to which hydrazine was added at some time latter after preparing the bath, started turning turbid. This observation could be explained on the basis of the fact that hydrazine can be oxidised by ferric ions and H_2O_2 [23,24].

Therefore, it is important to add hydrazine during the preparation of the bath itself. If the addition is made latter, hydrazine has a deleterious effect on bath stability.

Hydrazine sulphate thus added as one of the constituents (0.25 mol.l^{-1} to 0.8 mol.l^{-1}) of the bath gets depleted during plating and it is essential to estimate hydrazine content periodically and replenish it: for instance by oxidimetric titration of hydrazine using KBrO_3 as the oxidant and p-ethoxychrysodine as the indicator [25].

CONCLUSION

In the present study, the authors have investigated three reducing agents viz., iron powder, hydroxylamine and hydrazine sulphate for their influence on the stability of iron plating bath. The inferences drawn from the experimental observations are presented below:

1. Iron powder aggravates the instability of the iron plating bath. Polyferric sulphate is the major constituent of the fresh precipitate formed in the bath. Formic acid in the bath is decomposed and formation of iron (III) formate is identified as an intermediate step. Iron oxide alone or along with the iron polysulphate might be responsible for the formic acid decomposition.

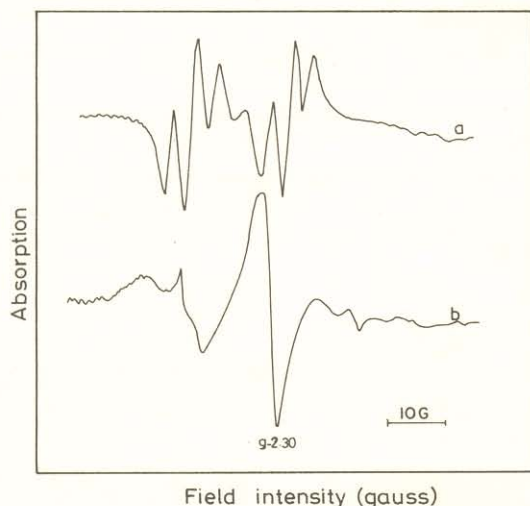


Fig. 3: Qualitative EPR spectra of
(a) hydroxylamine added fresh iron plating bath (b) the precipitate isolated from an aged hydroxylamine added bath

2. Hydroxylamine brings about a destructive effect upon addition to iron plating bath producing a swifter denser precipitate consisting of ferric sulphate and ferric oxide.
3. Hydrazine sulphate (0.25 mol.l^{-1} to 0.8 mol.l^{-1}) is found to be a good addition agent for improving the service life of iron plating bath. But formic acid should be absent in the bath. Otherwise some polymeric resins are formed. An optimum temperature of 323-333 K and a pH of 1 to 2 are found to enhance the beneficial role of hydrazine.
4. Hydrazine should be added as a constituent of the bath even while preparing the bath. A continuous check on the Hydrazine content during the plating process is essential. If the bath were starved of hydrazine and plating were carried out, then addition of hydrazine sulphate poisons the bath because it is oxidised by ferric ions.
5. The decomposition of formic acid as observed in the present study raises concern over its use in iron plating bath.

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