

The Influence of Temperature on the Co-deposition of Iron in Electro deposited Zinc Metal Films

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Abstract

The effect of substrate temperature on the co-deposition of iron in zinc films at different current densities and ferrous ion concentrations, were investigated systematically using atomic absorption technique for analyzing the film content from Zn and Fe. The co-deposited iron was not linearly dependent on bath temperature.

It was also found that the co-deposited iron suppresses markedly the electrowinning of Zn from sulfate solution at $T \leq 75^\circ\text{C}$.

The lowest value of the co-deposited iron was recorded at 95°C .

Such investigations have importance in electrowinning of Zn, storage batteries and in electrochemical catalysis.

Introduction

The bulk of all previous work (1-8) concerned with impurities in zinc baths have been devoted either to its effects on the mode of crystal growth specially the appearance of spongy growth , or to the faradic yields in Zn electrowinning from zinc chloride, or zinc alkaline baths. Both the iron (II) and the iron (III) ions as minor impurities in ZnCl_2 bath at low current densities ($1-100 \text{ mAcm}^{-2}$) were found neither co-deposit locally nor alloy with zinc, but they have a catalytic effect on the spongy growth of pure zinc (6, 7). Most of those investigations were carried out at very low current densities $I \leq 50 \text{ mA.cm}^{-2}$ and at low concentration of metal ions $\leq 10 \text{ ppm}$ at room temperature. This paper reports the influence of temperature on co-deposition of Fe with Zn in presence of Various Concentration of Fe (II) in acidic Zinc sulfate solution by using galvanostatic .

Experimental

Zinc was deposited galvanostatically from Zinc sulfate solution, containing certain amount of ferrous ions as impurities. The deposition cell was embedded in a thermostat for temperature control, within ± 1 C°. The anode was a zinc rod of purity (99.999%). L= 10cm, O.D.= 7mm. The solution was stirred and N₂ gas was passed through the solution before and during the deposition period. Zinc was deposited on a chemically polished copper foil (9) of an area of 1.0 cm². The deposition bath was composed of 1 mol/l (ZnSO₄. 7H₂O), 0.9826gm.l⁻¹ Na₂ So₄. 10H₂O and 15gm.l⁻¹ (NH₄)₂So₄. The Ph of the solution was 4.5. For every deposition a fresh Zn-Fe solution was added to a clean cell. After stabilizing the temperature in the cell the electrodeposition was followed. This sequence was repeated five times under the same conditions. Those samples were dissolved separately in 30% HNO₃ (AR). Later on they were diluted to 25ml, for chemical analysis which was conducted by atomic absorption technique in order to determine the film contents from Zn and Fe, with an accuracy of about ± 1 ppm for both elements.

Results and Discussion

Fig. (1) shows, the co-deposited iron in weight percentage increases with temperature at $\leq 75^\circ\text{C}$, current densities 40, 200 and 300mA.cm⁻² and 10 ppm Iron (II) concentration. This behavior is controlled by different factors:-

1-The depolarization of iron cathodic reduction (UPD, under potential iron deposition) due to an increase in the electrocatalytic effect with temperature, increases the Fe % in the zinc film.

2-The rate of hydrogen evolution (RHE) increases with increasing T, due to the lowering the overpotential for H₂ evolution (HE).

These two factors decrease the concentration of active sites for Zn reduction

and at the same time increases the redissolution of some of the already deposited zinc especially the adatoms due to the (formation) of the microgalvanic cells (MGC'S) at the border between iron, and the zinc grains.

This factor increases the Fe % in the film.

3-The burned black zinc (BB-Zn) increases with T at the early stages of

nucleation (7,9) this lead to appreciable increases in the- crystal defects, such as dislocation and surface roughness. These defects raise the concentration of active sites, especially the edges of screw dislocation, which are favored for iron (II) reduction.

4-The surface area of the deposited film increases exponentially with increasing of impurity content (6), which is typical for autocatalytic processes. This can also be accompanied by (HE), this phenomena has the same influence on Fe % as that referred in point (3). But at 100 mA cm^{-2} (Fig.1), the Fe % decreases linearly and slowly with T, i.e.. Due to more compact spongy growth at such current density (6,7,9), and also to the increases in crystal size with T at this I (9).

The concentration of active sites, therefore , decreases and Consequently lower the Fe % with T . Fig. 1 shows that the Fe % at $I \leq 100 \text{ mA cm}^{-2}$ is still higher than that measured at $I \geq 200 \text{ mA cm}^{-2}$. The reason for this behavior is mainly due to the spongy metallic deposits, (7) which grows as a function of time more than as a function of current density, therefore it grows at lower electrode reaction rates larger crystals with higher concentration of sharp edges and dislocations. This means the density of active sites preferred for iron reduction increases (7). But at $I \geq 200 \text{ mA/cm}^2$ the BB-Zn% increases at the early stages of deposition because the BB-Zn grows strictly as a function of I. Later on the (BB-Zn)stop growing after spreading to a limiting surface, then and at later stages the metallic growth spreads overall the surface (7). This led to an appreciable decreases in Fe % because the surface areas coated by (BB-Zn) provide active sites which are preferred for (HE)rather than for Iron (II) reduction. Further deposition time is very short at $I \geq 200 \text{ mA/cm}^2$. Therefore the percent of the re-dissolved zinc due to the (MGC'S) decreases. Moreover at $I \geq 200 \text{ mA/cm}^2$ the (HER)is much higher than that at lower I. Further the (HER) is much higher at the surface of the deposited iron grains due to a high Electro-catalytic effect of iron on (HE). This led to an appreciable delay in Fe reduction. At 27 C° the Fe % at $I \geq 200 \text{ mA cm}^{-2}$ is very low relative to the Fe % at lower I which is an experimental evidence for this interpretation. At 95 C° the Fe % is the least at all current densities and at all concentration of Fe^{2+} in the solution (Fig.1-4). This drastic decline in Fe % is due to the following factors:

1-At high T the crystals grown in the form of hexagonal platelets and the (hkli) direction of the crystal planes is $\langle 0001 \rangle$, this plane has the

lowest specific surface free energy σ has higher over potential for iron (II) reduction than those planes with higher σ such as $\langle 111 \rangle$ and $\langle 110 \rangle$. This factor seems to be decisive for reducing the Fe %.

2-At 95 C° iron was deposited on zinc anode, which was visually observable. Thus some of the iron was consumed at the anode surface this reduces its

reduction rate on the cathode. It seems here that the iron deposition on the anode surface was not compact as it was observed in the case of lead deposition on zinc anode (4). Thus the blocking of the active sites for zinc dissolution from the anode surface was not observed, while Pb blocked the zinc active sites on the anode.

3-The (HER) is a direct function of temperature and it arrives its maximum value at 95 C° relative to that at T<95> C°. The (HE) reduces the cathodic reduction of iron because the preferred active sites for iron are blocked by reduced H-atoms.

4- It is known (6,7) and our experimental results show, that the co-deposition of iron is not diffusion determinant process, but it is potential determinant. At 95C°, the applied potential required for passing the needed current density is highly reduced due to the appreciable increase in the cell solution conductivity. Therefore the iron depolarization reduced to a minimum value relative to that at T < 95 C°.

The sequence of the results in fig. 2 at 75°C differs than that in fig. 1-the highest Fe % at 75°C appears at 300mA cm⁻² followed by 40, 100 and 200mA/cm². This due to the fact that it requires a supply of higher potential for the very high values of I. This led to a higher is also known from the microscopic investigations (9,11) that the crystal deposition rate of Fe, since Fe reduction is potential dependent, its defects increase appreciably at a very high I. Therefore deposition of Fe increases and at the same time blocks the further zinc deposition because the same active sites which are favored by iron are also active for zinc reduction, this led to a further Fe reduction and Fe grain formation, this increases the Zn redissolution due to the formation of the (MGC 'S).

At T ≤ 50°C (fig .2), the Fe % is mostly smaller than that in fig. 1, this is due to a non local deposition of Fe on Zn, this rise the (HE) at the nucleated iron sites. It seems that the number of nuclei formed at the early stages of deposition is much higher at 50 ppm than that at 10 ppm, because as it seems and only at the early stages, the reduction

rate depends on Fe^{2+} concentration. Therefore an increase in the Fe nuclei increases the (HER) and at the same time depresses further the iron reduction in the later stages of deposition.

The results at $\text{CFe}^{2+} = 150\text{ppm}$ Fig.3 are another experimental evidence for the last interpretation which has same behavior as the results in fig. 1. But the results at $T \leq 50^\circ\text{C}$ in fig.3 are a little differs. The reason for the non-appreciable variation of Fe % in this T range is due to the lower redissolution of Zn due to (MGC'S), and also to the formation of smoother film surfaces grown at $T \leq 50^\circ\text{C}$ (9), than those grown at 70°C . The earlier discussion mentioned in relation to Fig. 1, must be taken in account in this interpretation.

The behavior of iron co-deposition in – Fig. 4 differs from that in figs 1,2,3. In general Fe % decreases with T. At 27°C the Fe % reaches its highest value at $40\text{mA}\cdot\text{cm}^{-2}$ this is due to the present of the present of very high concentration of Fe^{2+} in the Helmholtz double layer which led to the nucleation of a very high number of iron nuclei at the early stages of deposition. This great number of Fe nuclei led to the growing of iron grains with increasing in the time of deposition, this can take place at low T and low I, because the (HE) is strictly a function of I and T (5,6,7,9), therefore the (HE) at $40\text{mA}\cdot\text{cm}^{-2}$ and 27°C is very low compared with the HE at $I > 40\text{mA}\cdot\text{cm}^{-2}$ and $T > 27^\circ\text{C}$, the other reason of increasing Fe percentage % at $40\text{mA}\cdot\text{cm}^{-2}$ and 27°C is an increase in the rate of Zn redissolution from the cathode during deposition which is due to an appreciable increase In the number of (MGC'S). An experimental evidence for this interpretation is the sharp decay in Fe% at $T > 27^\circ\text{C}$. Such decay is due to an appreciable increase in (HE) with T. The growing of larger crystals with T decreases the number of defects and also the active sites preferred by Fe deposition.

The much lower Fe% at $I \geq 100\text{mA}\cdot\text{cm}^{-2}$ at $T \leq 50^\circ\text{C}$ than that at $40\text{mA}\cdot\text{cm}^{-2}$ is due to the fact that (HE) is a function of I. Therefore the (HE) at the Fe nuclei decline further Fe^{2+} reduction on their surfaces, and it is also due to the fact that hydrogen preferred the same active sites as those by Fe. Therefore we expect a low Fe%. The reason for decreases of Fe % with T and their low value at $T > 70^\circ\text{C}$ despite the presence of high concentration of iron ions in the solution is mainly due to the formation of Fe nuclei at the early stages of deposition. This increases markedly the (HER) at Fe centers with increasing both I and T. This prevents further increase in Fe^{2+}

reduction due to the depolarization of HE because of the electrocatalytic effect of both Fe and zinc active sites towards hydrogen reduction. The Fe% at 27°C and $I \geq 200 \text{mA.cm}^{-2}$ are low and lay near by each other, this behavior is agreed with earlier discussion were (HE) is much higher at those current densities, this decline markedly the Fe cathodic reduction.

But at 200mA.cm^{-2} and 50°C the Fe % is greater than that at 100°C and 300mA.cm^{-2} , this is mainly due to the higher (HER) at 300mA.cm^{-2} than that at 200mA.cm^{-2} , despite the presence of higher concentration of active sites, but the Fe% at 100mA.cm^{-2} is lower than Fe% at 200mA.cm^{-2} because of the smoother crystal surface grown at 100mA.cm^{-2} that prevents an increase in Fe% deposition due to higher amount of evolved hydrogen during this time. The low Fe% at $T > 70^\circ\text{C}$ is mainly due to the influence of temperature on further increasing in (HER). The deposition of iron on the anode surface at high temperature decreases the cathodic reduction of iron.

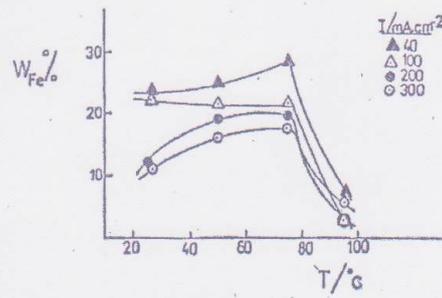


Fig.1: W_{Fe} % Versus substrate temperature
 Concentration of Fe(II)= 10 ppm

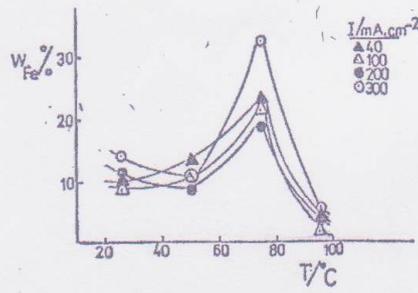


Fig.2: W_{Fe} % Versus substrate temperature
 Concentration of Fe(II)= 50 ppm

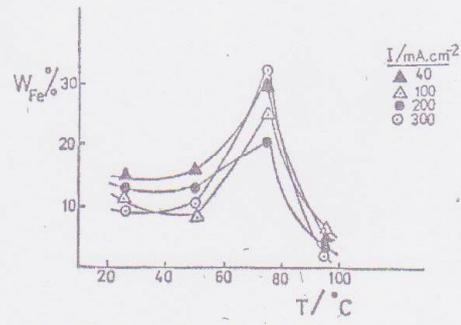


Fig.3: W_{Fe} % Versus substrate temperature
Concentration of Fe(II)= 150 ppm

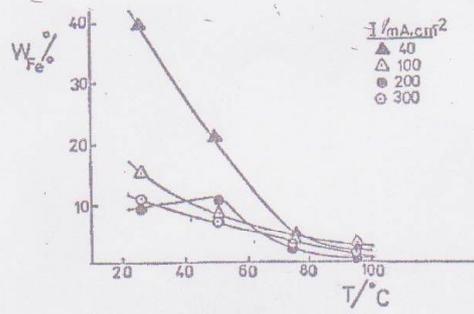


Fig.4: W_{Fe} % Versus substrate temperature
Concentration of Fe(II)= 300 ppm

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تأثير درجة الحرارة على الترسيب المشترك للحديد في رقائق فلز الخارصين المرسبة كهر وكيميائيا

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الخلاصة

تناولت الدراسة تأثير درجة الحرارة على نسبة الحديد المترسب مع الخارصين بوجود تراكيز مختلفة من ايونات الحديدوز في المحلول لكبريتات الخارصين . استخدمت تقنية الترسيب الكلفانوستاتيكي لهذا الغرض ، كما اجريت التحليلات باستخدام تقنية الامتصاص الذري لتحري ترسب الحديد والخارصين المشكلين للرقيقة المحضرة. لقد اتضح من نتائج هذه الدراسة ان نسبة الحديد المترسب مع الخارصين تعتمد وبشكل غير خطي على كل من الجهد ، معدل تحرر غاز الهيدروجين ، درجة الحرارة وعلى طبيعة نمو البلوري ، واتضح ان العلاقة بين نسب الحديد ودرجة الحرارة لم تكن خطية وذلك لحدوث اكثر من خطوة في ان واحد على سطح الكاثود اثناء عملية الترسيب . كما ثبت من النتائج التجريبية ان نسب الحديد المترسب مع الخارصين كانت اوطأ ما يمكن عند درجة ٩٥ م° بغض النظر عن كثافة التيار المستخدم او تركيز ايونات الحديد(II) في المحلول .