

Catalytic Effect of Cl^- on Electrodeposition of Binary Zinc Alloys With Iron-group Metals

YIN Ren-he^{*}, FANG Zheng-hua, CAO Wei-min, A. ZAKARIA, ZHOU Rong-ming
(Shanghai Univ., Shanghai Bao shan, 200436, China)

Abstract: Zinc-iron-group metal alloys were deposited under coulstatic (10C. cm^{-2}) at 40 chloride baths. The deposited alloys were quantitatively analyzed by Atomic Absorption Spectrometry. The current efficiency, percent content and partial polarization curves were obtained by the results. The morphology of the deposits was observed by means of Scanning Electron Microscopy (SEM). We observe that the electrodeposition of zinc-iron-group metal alloys is one of the best known examples of anomalous codeposition. We found the catalytic effect of Cl^- on the electrodeposition behavior of iron-group metal. Overpotential of iron-group metal dropped abruptly at high Cl^- concentration, while transition current density of Zn increased gradually.

Key words: Zinc-iron-group metal alloys, Anomalous codeposition, Catalytic effect, Transition current density.

CLC number: O 646.5, TQ 153.2

Document Code: A

1 Introduction

It is known that the protective value of zinc is partially a result of its ability to form a protective film when plated on a base metal, such as steel. Although pure zinc coating provides some degree of protection for the substrate, zinc is consumed rapidly in a severe corrosion environment. Consequently, we develop zinc alloys, such as zinc-nickel^[1], zinc-cobalt^[2] and zinc-iron^[3], which provide better protection than pure zinc coating. These alloy systems offer superior corrosion resistance and mechanical properties, weldability, paintability and thinner coating. The corrosion resistance of zinc-iron-group alloys is related to the iron-group metal content. Because there is little attention being paid on the catalytic effect of Cl^- on the electrodeposition of zinc-iron-group

Received date: 2 Jun. 2000, accept date: 14 Aug. 2000

^{*} To whom correspondence should be addressed.

Foundation item: Sponsored by State Key Lab for Phys. Chem. of Solid Surface, Xiamen Univ.

metal alloys, we decide to examine the electrodeposition behavior of zinc-iron-group metal alloys from chloride baths.

2 Experimental

The electrodeposition of zinc-iron-group metal alloys was obtained on a copper cathode of $1 \times 1 \text{ cm}^2$ under coulstatic ($10 \text{ C} \cdot \text{cm}^{-2}$), galvanostatic and unagitated conditions. Plating baths consisted of chloride of each metal (). In Zn-Fe plating bath contained a small amount ($1 \text{ g} \cdot \text{l}^{-1}$) of sodium citrate to prevent ferric formation. Insoluble platinum anode was used for the codeposition. The reference electrode was $\text{Hg} / \text{Hg}_2\text{SO}_4$. The current density was widely varied from 0.01 to $200 \text{ A} / \text{dm}^2$ at 40°C . The deposited alloys were dissolved from the cathode with nitric acid. Each metal was quantitatively analyzed by Atomic Absorption Spectrometry. The morphology of the deposits was observed by means of Scanning Electron Microscopy (SEM).

3 Results and Discussion

Fig. 1 gives experimental results showing the effect of current density on content of iron-group metal and cathode current efficiency at $\text{pH} = 3$ from chloride baths. The broken line in the figure indicates the composition reference line (CRL), which shows when the weight-percentage composition of the alloy just equals the metal-percentage in the bath. In the case in which iron-group metal content of the alloy lies above the CRL, alloy deposition of normal type occurs, because the alloys contain a large ratio of more noble iron-group metal to Zn, indicating the preferential deposition of more noble metal. On the other hand, iron-group metal contents below the CRL represent anomalous type alloy deposition, in which the preferential deposition of less noble Zn. In fig. 1, When Cl^- concentration increases, region which lies below CRL becomes small. It indicates that the preferential deposition of less noble Zn tends to be hard with increase of Cl^- concentration and iron-group metal content of the alloy in the anomalous codeposition region keeps high. Fig. 2 shows partial polarization curve of Ni, Co, Fe. From partial polarization curve of iron-group metal, overpotential of iron-group metals drops abruptly at high Cl^- concentration. Thus its content of the alloy increases. Figures 1 and 2 reveal the catalytic effect of Cl^- on the electrodeposition of iron-group metals.

Partial polarization curves of Ni, Co and Fe in the solution containing their corresponding metal ions at different Cl^- concentrations, turn to be similar to those of Ni, Co and Fe in zinc-iron-group metal alloy deposition. Taking Ni as an example to discuss catalytic mechanism of Cl^- . Equations (1) ~ (3) were explained by Bockris^[4] mechanism. Equation (2) which produces $(\text{NiOH})_{\text{ad}}$ (adsorbent) is the rate-determined step. Thus, electrochemical polarization carries on during electrodeposition process. Deposition of iron-group metal needs large overpotential and anomalous codeposition that preferential deposition of Zn occurs.



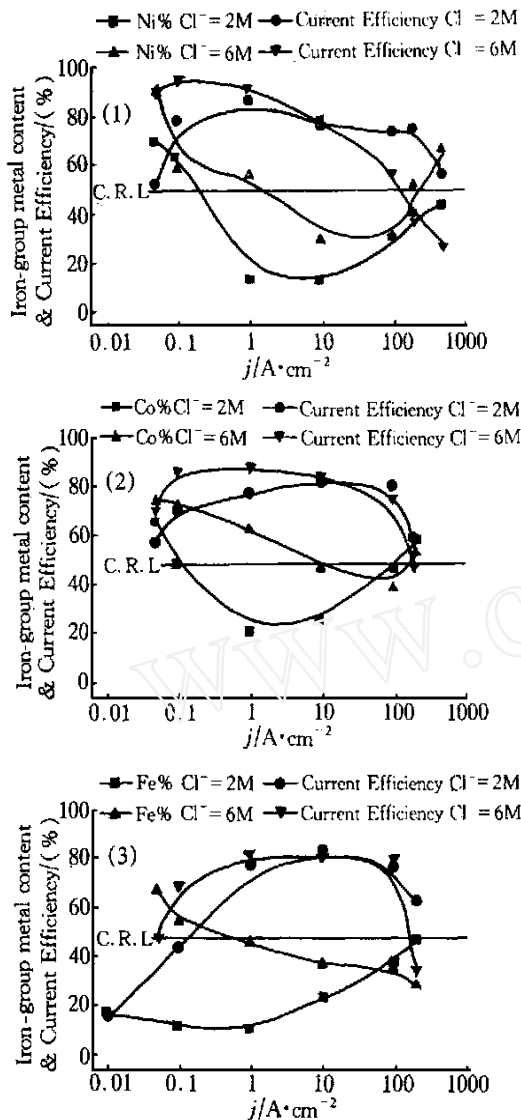


Fig. 1 Effect of current density on content of iron-group metal and current efficiency
(1) Zn-Ni (2) Zn-Co (3) Zn-Fe

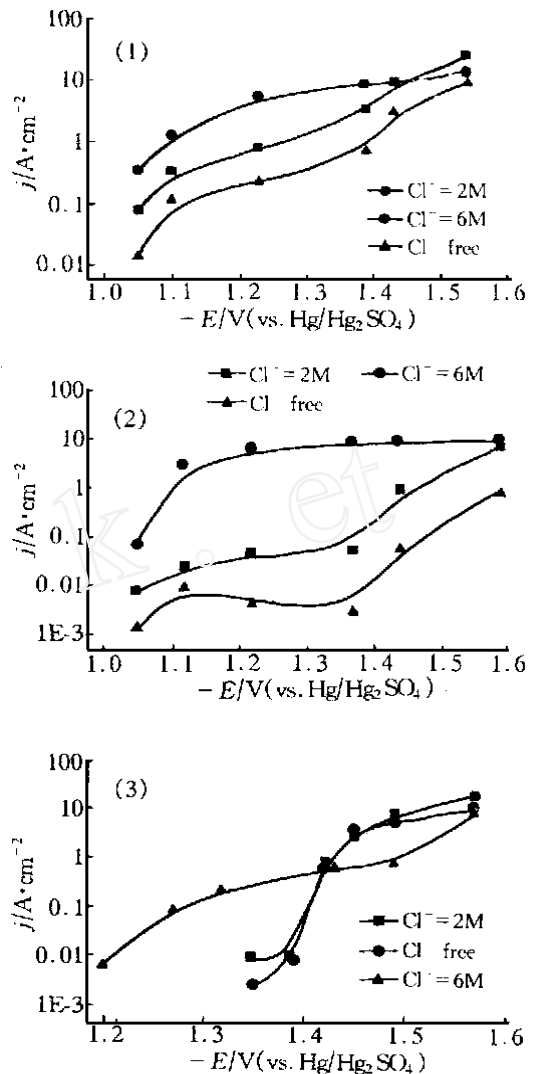
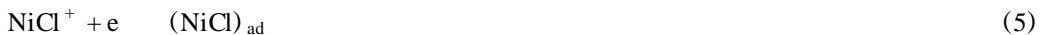


Fig. 2 Partial polarization curves of Ni, Co, Fe in zinc-iron-group metal alloy deposition
(1) Ni (2) Co (3) Fe



While Cl^- existed in the solution, Equations(4) ~ (6) described the deposition of Ni report-

ed by Yashuda et al^[5]. Equation(5) is the rate-determined step and $(\text{NiCl})_{\text{ad}}$ is the adsorbent, which makes deposition of Ni easy and Zn content of the alloy deposition decreases. We will get the similar results from the experiment of Co and Fe. Our results corresponded to these mechanisms discussed above.

Fig. 3 shows polarization curves of H_2 in the solution without any metal ions. Hydrogen overpotential rises with increase of Cl^- concentration, which inhabits hydrogen discharge. Because of inhabitation of hydrogen discharge, the pH near the cathode doesn't reach a critical value for the formation of a zinc hydroxide film. Thus deposition of iron-group metal is easy to be carried out. We can know catalytic effect of Cl^- on the iron-group metal deposition indirectly.

Fig. 4(a-c) are typical surface morphologies taken by SEM. With an increase of Cl^- concentration, an extremely compact and homogeneous surface from picture(a) to (c) was evident. The internal stress occurred on the surface seen in picture(c). These photos are in accordance with Fischer's mechanism. Fischer^[6] reported that with addition of Cl^- , activation energy for crystallization decreased, the grain size of the deposits compacted and even the internal stress occurred in the end. The internal stress caused by the volume contraction and close packing of atoms. Thus catalytic effect of Cl^- will be seen indirectly from these photos taken by SEM.

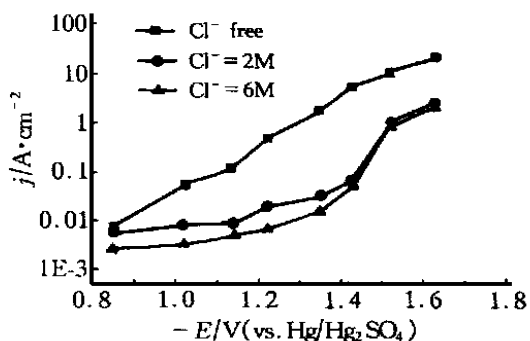


Fig. 3 Partial Polarization Curves of H_2 in the solution without any metal ions at Ni electrode

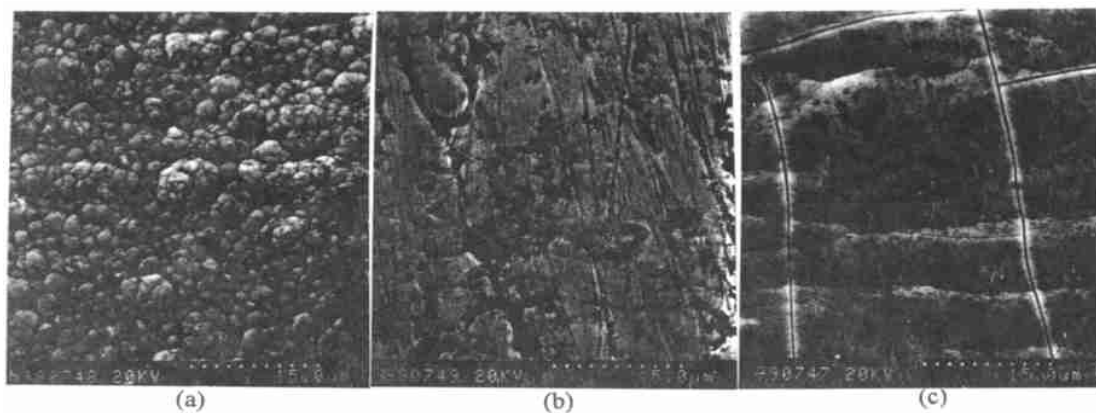


Fig. 4 SEM micrographs for Zn-Ni coating at different Cl^- concentration

(a) Cl^- free (b) $\text{Cl}^- = 2 \text{ mol/L}$ (c) $\text{Cl}^- = 6 \text{ mol/L}$

In conclusion, at higher current efficiency, alloy deposition of anomalous type occurs.

Catalytic effect of Cl^- on deposition of iron-group metals will be found in our experiments. Catalytic effect of Cl^- is discussed that in case of increase of Cl^- concentration, deposition of iron-group metal is much easier to occur.

References:

- [1] R. Albalat, E. Gomez, C. Muller, J. Pregonas, M. Saret, E. Valles. Electrodeposition of Ni-Zn alloys and their thermodynamic evaluation[J]. J. Applied. Electrochemistry, 1991, 21, 44~49.
- [2] W. M. J. C. Verberne. Mechanism of the electrodeposition of zinc alloys containing a small amount of cobalt[J]. Trans. IMF, 1986: 64,30.
- [3] N. Zaki. Mechanism of the electrodeposition of zinc with iron-group metals from sulfate baths[J]. Metal Fin, 1989, 87(6): 57~60.
- [4] J. O. M. Bockris, G. A. Ranzummany. Fundamental aspects of electrocrystallization[M]. New York: Plenum Press, 1967, Chap. 9.
- [5] Mitsuhiro Yasuda Izumi Ohno, H. Shiro Role of chloride ion on nickel plating[J]. J. ISIJ. 41, 1990: 312.
- [6] H. Fischer. Electrocrystallization and electrolytic deposition mechanism for metal deposition[J]. J. Electrochem. Soc., Japan, 1967, 35, 109.

Cl^- 对 Zn-Fe 族元素二元合金 共沉积的催化作用

印仁和, 方正华, 曹为民, A. ZAKARIA, 周荣明

(上海大学理学院化学系, 上海 宝山, 200436)

摘要: 在氯化物电解液中以定电量 ($10\text{C} \cdot \text{cm}^{-2}$), 恒温 40°C 电沉积 Zn-Fe 族元素二元合金. 沉积产物用原子吸收光谱分析. 根据分析结果, 作出相应的电流效率、百分含量及部分极化曲线. 镀层形貌采用扫描电镜 (SEM) 观察, 发现: Zn-Fe 族元素合金的共沉积为异常共沉积. Cl^- 对铁族元素有催化作用. 随着 Cl^- 浓度的增加, 降低了铁族元素的过电位, 促进了铁族元素金属的沉积.

关键词: Zn-Fe 族元素合金; 异常共沉积; 催化作用; 转移电流密度