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碱土金属离子与 EDTA 对纯铝在碱性溶液中的协同缓蚀作用

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摘要　通过集气实验、极化曲线和电化学阻抗谱等方法研究了碱土金属离子与乙二胺四乙酸(EDTA)对纯铝在 4 mol·L⁻¹ KOH 溶液中的协同缓蚀作用. 实验结果表明铝在含 0.02 mol·L⁻¹ EDTA 和饱和 Ca(OH)₂、Sr(OH)₂ 的溶液中具有最小的腐蚀速率. EDAX 分析表明碱土金属离子和 EDTA 没有参与到铝表面氧化膜的组成中, 说明缓蚀剂是通过吸附在铝表面起作用的, 这表明它们是界面型缓蚀剂而非相间型缓蚀剂.

关键词：　纯铝，　碱性溶液，　腐蚀，　碱土金属，　EDTA，　缓蚀剂

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The Cooperative Inhibition Effects of Alkaline Earth Metal Ions and EDTA on the Corrosion of Pure Aluminum in an Alkaline Solution

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Abstract　The cooperative effects of alkaline earth metal ions and EDTA (ethylenediamine tetraacetic acid) on the corrosion inhibition of pure aluminum in 4 mol·L⁻¹ KOH solution were investigated by hydrogen collection, polarization curve and electrochemical impedance spectroscopy(EIS). It was found that aluminum exhibits minimum corrosion rate in 4 mol·L⁻¹ KOH solution containing 0.02 mol·L⁻¹ EDTA, saturated Ca(OH)₂ and saturated Sr(OH)₂. EDAX analysis showed that alkaline earth metal ions and EDTA have no contribution to the formation of the surface film on aluminum. Therefore the inhibition effect may be caused by the adsorption of the inhibitor on aluminum surface. This fact indicates that these two ions act as interface inhibitors rather than inter-phase ones.

Keywords：　Pure aluminum,　Alkaline solution,　Corrosion,　Alkaline earth metal,　EDTA,　Inhibitor

Aluminum seems to be a potentially attractive anode material for electrochemical power sources with high energy densities[1-4], due to its low atomic weight and ability to transfer three electrons per atom, combined with high negative standard electrode potential. In order to obtain high current density, it is advantageous to use alkaline solution. However, aluminum undergoes a parasitic corrosion reaction, resulting in the evolution of hydrogen and the decrease of the anode utilization. Earlier efforts were made to modify the electrolytes by adding additives to make the electrolytes less corrosive[5-6]. A set of aliphatic and aromatic aldehydes was examined for their effectiveness in preventing the corrosion of aluminum alloy (2S) in 1 mol·L⁻¹ NaOH solution and their influence on the anodic polarization behavior[7]. MacDonald *et al.*[1] employed SnO₃²⁻, In(OH)₃, BiO₂²⁻, Ga(OH)₄⁻, MnO₄²⁻, and binary combinations in alloys BDW(Al-1Mg-0.1 In-0.2Mn) and 21(Al-0.2Ga-0.1In-0.1Tl), and found that K₂MnO₄

and $Na_2SnO_3+In(OH)_3$ were effective inhibitor systems. It was found that the addition of zinc oxide to alkaline solution significantly reduced the corrosion of aluminum electrode[8-9]. In the efforts to decrease the corrosion rate of aluminum, it was also found that calcium ions in combination with certain complexes are helpful[10-14]. In the present study the influences of alkaline earth metal hydroxide alone and in combination with EDTA in 4 $mol \cdot L^{-1}$ KOH solution were investigated by means of hydrogen collection, polarization curves and electrochemical impedance spectroscopy, and the aluminum surface was subsequently observed by SEM and analyzed by EDAX.

1   Experimental methods

Electrochemical measurements were carried out in a classical three-electrode glass cell. The working electrode was made of specpure aluminum rod, 6.35 mm in diameter. The electrode surface was polished by 1000# waterproof abrasive paper, degreased in acetone and rinsed in deionized water. The counter electrode was a platinum foil and the reference electrode was a Hg/HgO electrode. All the solutions were prepared by reagents of A.R. grade and deionized water. The measurement system consists of a potentiostat (EG&G model 273A) and a lock-in amplifier (model 5210), controlled by a microcomputer with certain software. The potentiodynamic polarization curves were measured at a scanning rate of 1 $mV \cdot s^{-1}$ and in the potential range from −2100 mV to −1000 mV (*vs* Hg/HgO). Electrochemical impedance spectroscopy (EIS) was obtained in the frequency range of 100 kHz to 10 mHz and at a.c. signal amplitude of 5 mV. All the above measurements were taken at 25 ℃. Before each measurement the electrode was kept in test solution for no less than half an hour, during which a steady open circuit potential was obtained. SEM and EDAX analyses were performed with an FEI SIRION SEM system, before which the specimens were kept immersed in the solutions for eight hours, then rinsed in deionized water and dried in air.

2   Results and discussion

The corrosion current densities can be calculated by the results of hydrogen collection at OCP(open circuit potential), as described in Ref.[14]. Table 1 shows the calculated corrosion current densities and inhibition efficiencies of pure aluminum in 4 $mol \cdot L^{-1}$ KOH solution containing alkaline earth metal hydroxides and EDTA with different concentrations. In this solu-

tion, the alkaline earth metal ions are almost completely chelated by EDTA, and the concentrations of free ions are low because of the high concentration of OH^-. Therefore the total concentrations of alkaline earth metal ions are almost equal to that of EDTA. It can be seen from Table 1 that the current density is greatly decreased by the addition of $Ca(OH)_2$ and $Sr(OH)_2$, and their inhibition effects are further enhanced by the addition of EDTA, while EDTA itself has only a little inhibition effect. When the concentration of EDTA is 0.01 $mol \cdot L^{-1}$, $Ca(OH)_2$ and $Sr(OH)_2$ respectively show the largest effect. Saturated $Ca(OH)_2$ is found to show largest inhibition effect among alkaline earth metal hydroxides followed by other hydroxides in the order $Ca(OH)_2 > Sr(OH)_2 > Ba(OH)_2 > Mg(OH)_2$. And when added with 0.01 $mol \cdot L^{-1}$ EDTA, they also follow the above order. It is believed that the cooperative action of alkaline earth metal ions and EDTA may be due to the formation of a chelate complex between cations and EDTA[15]. And the chelate complex might be physically adsorbed, with cations disposed towards the metal surface.

The results of the polarization curves show that the OCP shifts to the positive direction in saturated $Sr(OH)_2$-containing

Table 1   The corrosion current densities and inhibition efficiencies of pure aluminum in 4 $mol \cdot L^{-1}$ KOH with inhibitors calculated by hydrogen evolution

Electrolyte	i_{corr} / ($mA \cdot cm^{-2}$)	η (%)
blank (4 $mol \cdot L^{-1}$ KOH)	16.24	0.0
+ 0.001 $mol \cdot L^{-1}$ EDTA	16.14	0.6
+ 0.005 $mol \cdot L^{-1}$ EDTA	14.81	8.8
+ 0.01 $mol \cdot L^{-1}$ EDTA	10.06	38.0
+ saturated $Mg(OH)_2$	15.48	4.7
+ saturated $Ca(OH)_2$	3.82	76.5
+ saturated $Sr(OH)_2$	4.88	70.0
+ saturated $Ba(OH)_2$	10.20	37.2
+ saturated $Mg(OH)_2$ + 0.01 $mol \cdot L^{-1}$ EDTA	8.97	44.8
+ saturated $Ba(OH)_2$ + 0.01 $mol \cdot L^{-1}$ EDTA	6.50	60.0
+ saturated $Sr(OH)_2$ + 0.001 $mol \cdot L^{-1}$ EDTA	4.68	71.2
+ saturated $Sr(OH)_2$ + 0.005 $mol \cdot L^{-1}$ EDTA	4.59	71.7
+ saturated $Sr(OH)_2$ + 0.01 $mol \cdot L^{-1}$ EDTA	3.94	75.7
+ saturated $Sr(OH)_2$ + 0.02 $mol \cdot L^{-1}$ EDTA	4.00	75.4
+ saturated $Ca(OH)_2$ + 0.005 $mol \cdot L^{-1}$ EDTA	3.41	79.0
+ saturated $Ca(OH)_2$ + 0.01 $mol \cdot L^{-1}$ EDTA	2.89	82.2
+ saturated $Ca(OH)_2$ + 0.02 $mol \cdot L^{-1}$ EDTA	3.08	81.0
+ saturated $Ca(OH)_2$ + saturated $Sr(OH)_2$ + 0.01 $mol \cdot L^{-1}$ EDTA	2.22	86.3
+ saturated $Ca(OH)_2$ +saturated $Sr(OH)_2$ + 0.02 $mol \cdot L^{-1}$ EDTA	2.10	87.1

solution (Fig.1a), while it shifts to the negative direction in saturated Ca(OH)$_2$-containing solution (Fig.1b). It can also be seen from Fig.1a that both the anodic and cathodic processes of aluminum in the solution with saturated Sr(OH)$_2$ are inhibited. But with increasing concentration of EDTA, the inhibition effect on the former is much greater than that on the latter. While in saturated Ca(OH)$_2$-containing solution, with increasing the concentration of EDTA, the inhibition effect on the latter is much greater than that on the former. This indicates that most strontium-EDTA chelate complexes may adsorb on the anodic active sites and the
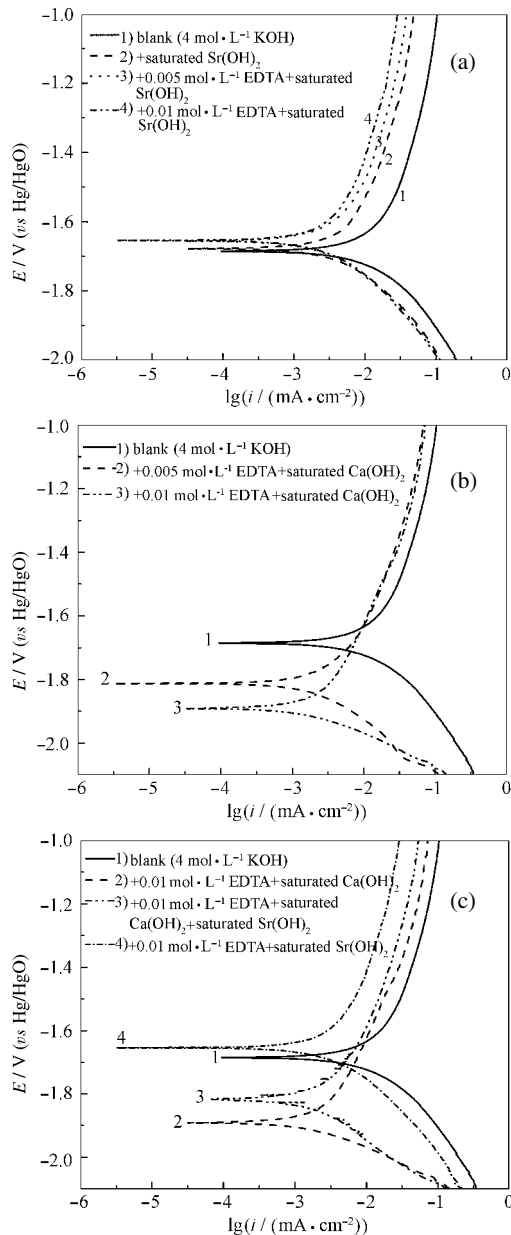

Fig.1 Polarization curves of Al in 4 mol·L^{-1} KOH solutions with or without additives

(a) EDTA+Sr(OH)$_2$; (b) EDTA+Ca(OH)$_2$;

(c) EDTA+Ca(OH)$_2$+Sr(OH)$_2$

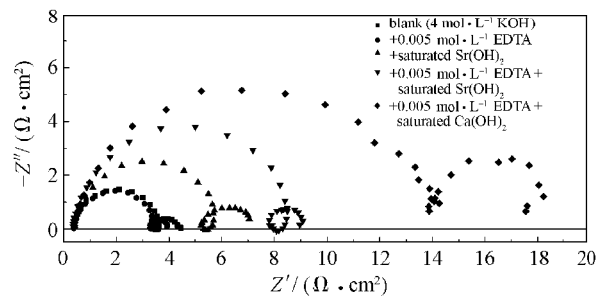**Fig.2 EIS of pure aluminum in 4 mol·L^{-1} KOH solutions with or without additives**

corrosion of pure aluminum in this solution is under anodic control, while calcium-EDTA chelate complexes may adsorb on the cathodic sites. Fig.1c indicates that the corrosion current density can be further decreased when saturated Sr(OH)$_2$ is added to the saturated Ca(OH)$_2$ containing solution, which can be attributed to the adsorption of the chelate complexes on both anodic active sites and cathodic active sites. The results of polarization curves are in agreement with those obtained by hydrogen collection.

Fig.2 shows the EIS of aluminum in 4 mol·L^{-1} KOH with or without additives at open circuit potential. These EIS patterns are similar, which indicates that the additives do not change the reaction mechanism of aluminum in the alkaline solution. The EIS patterns consist of three parts: a high-frequency capacitive loop, a middle-frequency inductive loop and a low-frequency capacitive loop. The high-frequency capacitive loop is caused by a charge transfer resistance in parallel with a double-layer capacitance. The inductive loop can be attributed to the adsorbed intermediate, and the low-frequency loop may be due to the growth and dissolution of the surface film[13-14, 16]. It can be found that the addition of saturated Sr(OH)$_2$ or Ca(OH)$_2$ and EDTA increases the charge transfer resistance. As shown in Table 1, the hydrogen evolution current density is greatly reduced in the solution with them. The model for the essential features of the electrode is represented by the electrical equivale nt circuit
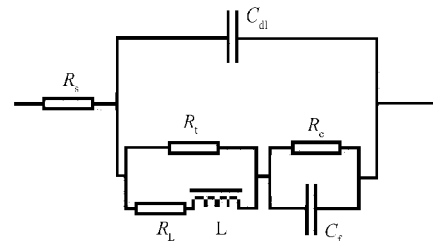

Fig.3 The equivalent circuit model of the aluminum electrode system

Table 2   Some parameters fitted from the EIS in Fig.2

Solution	$R_t / (\Omega \cdot cm^2)$	$10^6 \times CPE\text{-}Y(\Omega^{-1} \cdot cm^{-2})$	CPE-n
blank(4 mol·L^{-1} KOH)	3.31	7.0722	0.94051
+ 0.005 mol·L^{-1} EDTA	3.12	8.2656	0.93615
+ saturated Sr(OH)$_2$	5.52	7.4631	0.93040
+ saturated Sr(OH)$_2$ + 0.005 mol·L^{-1} EDTA	8.44	8.5048	0.92597
+ saturated Ca(OH)$_2$ + 0.005 mol·L^{-1} EDTA	12.18	15.621	0.89110

shown in Fig.3, where R_s is the total ohmic resistance of the solution, CPE is the constant phase element related to the double layer capacity, R_t is charge transfer resistance of the electrode. Table 2 shows some fitted parameters of EIS. The fitted data (R_t values) accord with the foregoing discussion.

After being kept immersed in 4 mol·L^{-1} KOH solution with additives for 8 h, the electrode surface was observed by SEM and examined by EDAX. Only aluminum and oxygen were detected by EDAX, with a ratio about 2:3, which indicated that the passive film contained only Al$_2$O$_3$. Alkaline earth metal was not found to participate in forming film. This fact indicates that alkaline earth metal ions-EDTA chelate complexes are interface inhibitors rather than inter-phase ones and they may produce inhibition effect by adsorbing on the active sites of aluminum electrode.

3   Conclusions

The corrosion of aluminum in 4 mol·L^{-1} KOH solution can be greatly inhibited by the addition of alkaline earth metal hydroxides, and calcium hydroxide is found to give largest inhibition effect. Their inhibition is enhanced by the addition of EDTA, while EDTA itself has only a little inhibition effect. The analyses on EIS and EDAX reveal that alkaline earth metal ions and EDTA chelate complexes may produce the inhibition effect on the corrosion of aluminum by adsorbing on the active sites of aluminum surface.

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