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Anodic Behavior of Zn22Al Alloy, Doped with Erbium

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Abstract. The article presents the results of a potentiodynamic study of the anodic behavior of the Zn22Al alloy with erbium dopants in various corrosive media of HCl, NaCl and NaOH electrolytes. Erbium alloying additions corrosion rate in various corrosive environments. In this case, there is a shift in the potentials in amounts of 0.01÷1.0 wt.% somewhat increase the anode resistance of the Zn22Al alloy by reducing the of corrosion, pitting formation and repassivation of alloys to the region of positive values. The dynamics of changes in electrochemical potentials favorably affects the parameters of the corrosion resistance of alloys. Erbium additions monotonically reduce the corrosion rate of the anode Zn22Al alloy in various media.

Keywords: Zn22Al alloy, erbium, potentiodynamical research, corrosive environments, corrosion rate, anodic behavior.

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Анодное поведение сплава Zn22Al, легированного эрбием

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Аннотация. В статье приведены результаты потенциодинамического исследования анодного поведения сплава Zn22Al с легирующими добавками эрбия в различных коррозионных средах электролитов HCl, NaCl и NaOH. Легирующие добавки эрбия в количествах 0.01÷1.0 мас.% несколько повышают анодную устойчивость сплава Zn22Al за счет уменьшения скорости коррозии в различных коррозионных средах. При этом наблюдается смещение потенциалов коррозии, питтингообразования и репассивации сплавов в область положительных значений. Динамика изменения электрохимических потенциалов благоприятно влияет на параметры коррозионной стойкости сплавов. Добавки эрбия монотонно снижают скорость коррозии анодного сплава Zn22Al в различных средах.

Ключевые слова: сплав Zn22Al, эрбий, потенциодинамическое исследование, коррозионные среды, скорость коррозии, анодное поведение.

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Introduction

The role of zinc coatings for protecting steel from marine, atmospheric and underground corrosion in neutral salt solutions is great. However, zinc deficiency, as well as an increase in the rate of zinc corrosion due to environmental pollution, aroused interest in replacing zinc coatings with zinc-aluminum ones [1–4]. Significant zinc savings when using such coatings, associated with a lower aluminum density, as well as their higher corrosion resistance under various conditions, led to the development of an industrial technology for producing steel sheets with a hot Zn–Al coating [5–8].

The practical use of anode coatings to protect metal structures from corrosion depends on the features of the alloy structure, surface condition, temperature, and properties of the alloy itself [9–11]. The most promising is the increase in the aluminum content in the Zn-Al alloy (for example, Zn55Al) [10] and the transition in phase composition to α – solid solution according to the state diagram [9]. However, this raises the risk of passivation of the aluminum component of the alloy. In this regard, the possibility of activating this alloy by introducing microadditives of the third component into its composition was considered [12–23]. It is known that rare earth metals are used as alloying additives to increase the corrosion resistance of Zn5Al and Zn55Al alloys [24–26].

Taking into account the effective feature of rare-earth elements [26], in this study we studied the effect of erbium dopants on the anodic behavior of the Zn22Al alloy in various corrosive media of HCl, NaCl, and NaOH electrolytes.

Experimental part

The starting material used was granulated zinc of the chemically pure grade, aluminum of the A7 grade and alloys of aluminum with erbium (10 wt% Er). From these metals alloys were obtained in corundum crucibles, in an electrical resistance furnace – SHOL, in the temperature range of 700–850 °C. From each heat, rods 8 mm in diameter and 140 mm long were cast into a graphite mold, the lower part of which was covered with a corrosion-resistant varnish, which made it possible to investigate the same prepared surface area of the alloy in all samples.

Potentiodynamical study [27, 28] of the anodic behavior of the Zn22Al alloy with dopants of erbium was carried out in various corrosive media of electrolytes HCl (0.001, 0.01, 0.1n), NaCl (0.03, 0.3, 3 %) and NaOH (0.001, 0.01, 0.1n). The potential sweep rate during potentiodynamic polarization on a PI-50.1.1 potentiostat was 2 mV/sec. The reference electrode was silver chloride, and the auxiliary electrode was platinum.

Results and discussion

The results of the corrosion-electrochemical study are presented in the Tables 1–3. As can be seen, over time, the free corrosion potentials ($-E_{cor.}$, B) of the alloys shift to the positive region. Potential $E_{free\ cor.}$ of the Zn22Al alloy doped with erbium as the concentration of chloride and hydroxide ion in the solutions of the studied electrolytes increases, it shifts to the region of negative values (Table 1). The introduction of erbium into the Zn22Al alloy within the studied concentration contributes to a shift in the potentials of corrosion ($-E_{corr.}$, B), pitting ($-E_{p.f.}$, B) and repassivation ($-E_{rep.}$, B) to the region of positive values. The potentials of corrosion, pitting formation and repassivation of alloys alloyed with

Table 1. Change in free corrosion potential ($-E_{free\ cor.}$, V) of the Zn22Al alloy with erbium, over time, in acidic, neutral and alkaline media

Media	Er additives in the alloy, wt.%	Alloy holding time, minutes							
		1/3	2/3	1	5	15	30–40	50	60
0.01n HCl	-	1.080	1.078	1.070	1.072	1.068	1.053	1.053	1.053
	0.01	1.024	1.023	1.022	1.020	1.017	1.015	1.015	1.015
	0.05	1.042	1.041	1.040	1.028	1.020	1.020	1.020	1.020
	0.1	1.054	1.053	1.052	1.045	1.039	1.033	1.033	1.033
	0.5	1.061	1.060	1.058	1.058	1.043	1.040	1.040	1.040
	1.0	1.072	1.072	1.071	1.064	1.055	1.045	1.045	1.045
0.3 % NaCl	-	1.021	1.019	1.018	0.995	0.985	0.960	0.960	0.960
	0.01	0.962	0.961	0.960	0.935	0.910	0.874	0.874	0.874
	0.05	0.972	0.972	0.971	0.940	0.915	0.885	0.885	0.885
	0.1	0.986	0.985	0.985	0.945	0.920	0.902	0.902	0.902
	0.5	0.994	0.993	0.992	0.950	0.925	0.912	0.912	0.912
	1.0	1.004	1.004	1.003	0.959	0.940	0.925	0.925	0.925
0.01n NaOH	-	1.141	1.140	1.136	1.134	1.133	1.128	1.128	1.128
	0.01	1.099	1.098	1.097	1.085	1.077	1.066	1.066	1.066
	0.05	1.100	1.099	1.098	1.093	1.080	1.079	1.079	1.079
	0.1	1.104	1.103	1.102	1.095	1.097	1.085	1.085	1.085
	0.5	1.107	1.106	1.105	1.099	1.100	1.090	1.090	1.090
	1.0	1.110	1.109	1.108	1.100	1.100	1.100	1.100	1.100

Table 2. Anode characteristics of the Zn22Al alloy with erbium, in acidic and alkaline media

Media, n	Content Er in the alloy, wt.%	Electrochemical potentials, V				Corrosion rate	
		$-E_{fr.cor.}$	$-E_{cor.}$	$-E_{p.f.}$	$-E_{rep.}$	$i_{cor.}\cdot 10^2$ A/m^2	$K\cdot 10^3$ g/m$^2\cdot$h
0.001 HCl	-	1.023	1.250	1.038	1.043	0.055	0.564
	0.01	0.985	1.178	0.980	0.993	0.046	0.471
	0.05	0.990	1.190	0.992	1.000	0.047	0.482
	0.1	1.000	1.203	1.000	1.012	0.048	0.492
	0.5	1.008	1.219	1.015	1.026	0.052	0.533
	1.0	1.015	1.230	1.020	1.037	0.053	0.543
0.1 HCl	-	1.083	1.288	1.100	1.112	0.083	0.851
	0.01	1.040	1.230	1.070	1.085	0.066	0.676
	0.05	1.046	1.235	1.076	1.090	0.067	0.687
	0.1	1.051	1.250	1.081	1.094	0.068	0.697
	0.5	1.064	1.261	1.090	1.100	0.079	0.810
	1.0	1.070	1.270	1.095	1.107	0.080	0.820
0.001 NaOH	-	1.102	1.265	1.050	1.059	0.060	0.615
	0.01	1.039	1.215	1.016	1.021	0.050	0.512
	0.05	1.053	1.221	1.024	1.037	0.051	0.523
	0.1	1.061	1.230	1.030	1.042	0.052	0.533
	0.5	1.079	1.241	1.037	1.047	0.057	0.584
	1.0	1.081	1.254	1.045	1.052	0.058	0.594
0.01 NaOH	-	1.128	1.278	1.070	1.078	0.070	0.717
	0.01	1.066	1.236	1.036	1.040	0.060	0.615
	0.05	1.079	1.243	1.041	1.047	0.061	0.625
	0.1	1.085	1.251	1.049	1.054	0.062	0.635
	0.5	1.090	1.260	1.055	1.060	0.067	0.687
	1.0	1.100	1.265	1.060	1.071	0.068	0.697
0.1 NaOH	-	1.168	1.295	1.115	1.124	0.091	0.933
	0.01	1.109	1.259	1.080	1.087	0.071	0.728
	0.05	1.116	1.264	1.088	1.093	0.072	0.738
	0.1	1.128	1.272	1.094	1.099	0.073	0.748
	0.5	1.140	1.280	1.100	1.104	0.087	0.892
	1.0	1.156	1.285	1.105	1.111	0.088	0.902

erbium with an increase in the concentration of erbium in the range of 0.01–1.0 wt.% are shifted to the negative range of values. Erbium additions monotonically reduce the corrosion rate of the Zn22Al alloy in various media (Tables 2, 3). The dynamics of changes in electrochemical potentials favorably affects the parameters of the corrosion resistance of alloys in general.

The anodic branches of the potentiodynamical polarization curves related to alloys containing erbium (0.01–1.0 wt.%) are located below the curves of the zinc-aluminum alloy Zn22Al (curve 1), which indicates a decrease in the anodic dissolution of the alloys during alloying. Stabilization of

Table 3. Anode characteristics of the Zn22Al alloy doped with erbium in a neutral medium

Media, wt.%	Content Er in the alloy, wt.%	Electrochemical potentials, V				Corrosion rate	
		$-E_{fr.cor.}$	$-E_{cor.}$	$-E_{p.f.}$	$-E_{rep.}$	$i_{cor.} \cdot 10^2$	$K \cdot 10^3$
						A/m^2	$g/m^2 \cdot h$
0.03	-	0.920	1.068	0.810	0.815	0.039	0.399
	0.01	0.832	1.024	0.775	0.784	0.030	0.307
	0.05	0.845	1.032	0.782	0.790	0.031	0.318
	0.1	0.862	1.041	0.791	0.800	0.032	0.328
	0.5	0.887	1.055	0.800	0.807	0.036	0.369
	1.0	0.903	1.060	0.805	0.811	0.037	0.379
0.3	-	0.960	1.105	0.825	0.830	0.042	0.430
	0.01	0.874	1.051	0.789	0.797	0.034	0.348
	0.05	0.885	1.060	0.791	0.800	0.035	0.359
	0.1	0.902	1.079	0.800	0.807	0.036	0.369
	0.5	0.912	1.095	0.809	0.812	0.039	0.400
	1.0	0.925	1.100	0.818	0.826	0.040	0.410
3	-	0.993	1.133	0.845	0.850	0.048	0.492
	0.01	0.912	1.087	0.811	0.817	0.040	0.410
	0.05	0.926	1.092	0.819	0.823	0.041	0.420
	0.1	0.940	1.101	0.825	0.830	0.042	0.430
	0.5	0.950	1.112	0.830	0.836	0.045	0.461
	1.0	0.971	1.120	0.839	0.842	0.046	0.471

the anodic corrosion rate during polarization is achieved for low-alloy alloys. The dissolution current density from the passive state of the alloy with Er is lower than that of the Zn22Al alloy (Fig. 1).

The given data on the stabilization of the values of the free corrosion potential under changing external conditions make it possible to reveal its higher reproducibility compared to $E_{p.f.}$ and about the possibility of using $E_{rep.}$ independently as a criterion for the protective properties of oxide films. The repassivation potential is more stable and to a lesser extent than the pitting potential will depend on the composition of the solution and the state of the electrode surface. It should be noted that the definition of $E_{rep.}$ is more important for practical purposes, since it determines the range of potential values (Tables 1, 2) within which pitting is not formed.

The current density and corrosion rate of alloys alloyed with erbium increase with an increase in the concentration of chloride and hydroxide ions in the studied electrolytes. This phenomenon is noted for all alloy compositions. The influence of the content of chloride ions on the corrosion of alloys is associated with adsorption, which will rapidly lead to the formation of an outer layer of various phase oxides of adsorbed zincate compounds on the surface and in the pores of alloy samples.

With the addition of erbium of various concentrations in the Zn22Al alloy, the electrochemical inhomogeneity increases and the corrosion resistance is set by the amount and nature of the alloying element. The corrosion rate of alloys with erbium is somewhat lower than for the Zn22Al alloy. Erbium additions in the range of 0.01–0.1 % have a particularly positive effect, that is, it increases the anodic stability of the initial alloy in various corrosive environments. A further increase in the erbium

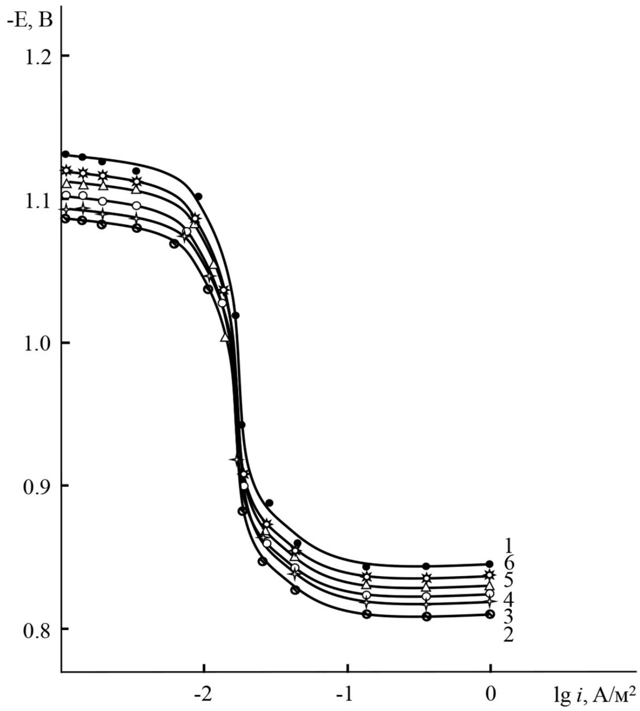

Fig. 1. Anode polarization curves of the Zn22Al alloy (1) containing erbium, wt%: 0.01 (2); 0.05 (3); 0.1 (4); 0.5 (5); 1.0 (6) in 3 % NaCl medium

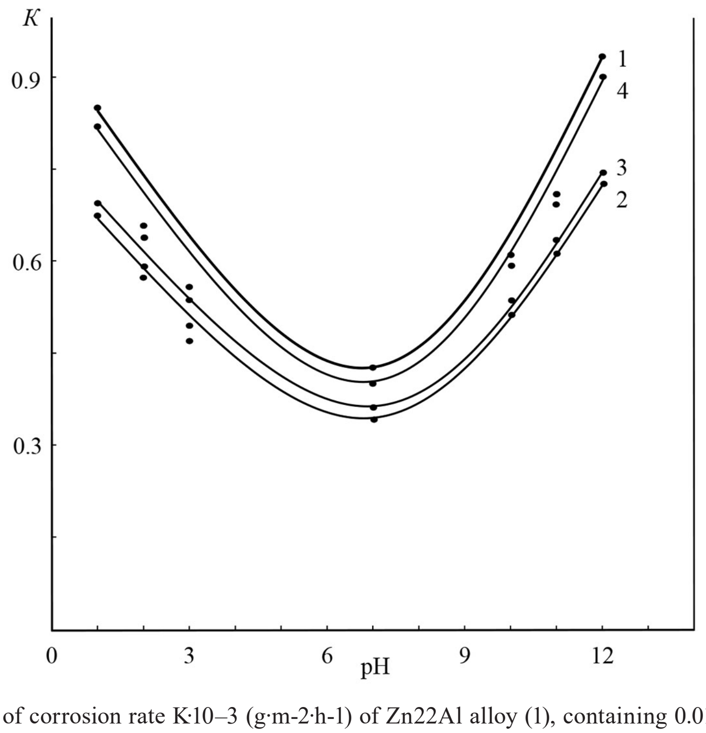

Fig. 2. Dependence of corrosion rate K·10–3 (g·m-2·h-1) of Zn22Al alloy (1), containing 0.01 (2), 0.1 (3) and 1.0 wt.% (4) erbium from the pH of the medium

concentration slightly increases the corrosion rate of the Zn22Al alloy, however, in absolute value it is less than that of the Zn22Al alloy. This dependence is observed in acidic, neutral and alkaline media at various pH values of the medium (Fig. 2).

Conclusions

Alloying zinc-aluminum alloy Zn22Al with erbium of various concentrations gives the alloy (protective coating) greater anodic stability in an acidic environment, due to their nature, thermodynamic stability or effective inhibition of one or another stage of the anode process due to the onset of a passive state.

The introduction of erbium (0.01–0.1 wt.%) into the Zn22Al alloy contributes to some decrease in the corrosion rate of the anode Zn22Al alloy. The compositions of these alloys are considered optimal in terms of the development of anodic alloy coatings for the protection of structures, products and structures made of carbon steel and cast iron from corrosion.

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