Journal of Siberian Federal University. Engineering & Technologies 2022 15(5): 561–568
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DOI: 10.17516/1999-494X-0417

УДК 669.017:620.193

Effect of Neodymium and Erbium on the Kinetics Oxidation of Zn0.5Al Zinc Alloy, in Solid State

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Received 18.04.2022, received in revised form 12.07.2022, accepted 15.08.2022

Abstract. Thermogravimetrical method studied the effect of alloying additions (on 0.01÷1.0 wt%) of neodymium and erbium on the oxidation kinetics of Zn0.5Al zinc alloy in the temperature range of 523–623 K. The values of the oxidation rate of the Zn0.5Al alloy and the alloy alloyed with neodymium and erbium, have been established in solid state. The behavior of ternary alloys with the participation of neodymium and erbium at the indicated temperatures somewhat differs from the oxidation of the binary Zn0.5Al alloy. For the eutectoid Zn0.5Al alloy, as compared with the alloys alloyed with neodymium and erbium, the minimum oxidation rate was noted. The addition of 0.5 and 1.0 % Nd and Er in the zinc alloy Zn0.5Al significantly increases its oxidizability. Alloy additions (on 0.01÷0.05 %) of neodymium and erbium slightly increase the oxidizability of the eutectoid zinc alloy Zn0.5Al. During the oxidation of the studied hard alloys, protective oxides pellicle are formed ZnO, Al_2O_3, Nd_2O_3, Er_2O_3, $ZnAl_2O_4$.

Keywords: alloy Zn0.5Al, neodymium, erbium, thermogravimetrical method, kinetics oxidation, activation energy.

Citation: Firuzi Hamroqul, Jobirov, U.R., Obidov, Z.R. Effect of neodymium and erbium on the kinetics oxidation of Zn0.5Al zinc alloy, in solid state. J. Sib. Fed. Univ. Eng. & Technol., 2022, 15(5), 561–568. DOI: 10.17516/1999-494X-0417

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Влияние неодима и эрбия на кинетику окисления цинкового сплава Zn0.5Al, в твердом состоянии

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Аннотация. Методом термогравиметрии изучено влияние легирующих добавок (по 0.01–1.0 мас.%) неодима и эрбия на кинетику окисления цинкового сплава Zn0.5Al, в диапазоне температур 523–623 K. Установлены значения скорости окисления сплава Zn0.5Al и легированного неодимом и эрбием сплава в твердом состоянии. Поведение тройных сплавов с участием неодима и эрбия при указанных температурах несколько отличается от окисления двойного сплава Zn0.5Al. Для эвтектоидного сплава Zn0.5Al, по сравнению со сплавами, легированными неодимом и эрбием, отмечена минимальная скорость окисления. Добавление по 0.5 и 1.0 % Nd и Er в цинковом сплаве Zn0.5Al существенно повышает его окисляемость. Легирующие добавки (по 0.01÷0.05 %) неодима и эрбия незначительно увеличивают окисляемость эвтектоидного цинкового сплава Zn0.5Al. При окислении изученных твердых сплавов образуются защитные оксидные пленки ZnO, Al_2O_3, Nd_2O_3, Er_2O_3, $ZnAl_2O_4$.

Ключевые слова: сплав Zn0.5Al, неодим, эрбий, термогравиметрический метод, кинетика окисления, энергия активации.

Цитирование: Ф. Хамрокул. Влияние неодима и эрбия на кинетику окисления цинкового сплава Zn0.5Al, в твердом состоянии / Ф. Хамрокул, У. Р. Джобиров, З. Р. Обидов // Журн. Сиб. федер. ун-та. Техника и технологии, 2022, 15(5). С. 561–568. DOI: 10.17516/1999-494X-0417

Introduction

The prospects for anticorrosion protection of carbon steel products and structures by only alloying metals are very small, as a result of which research is being carried out both in the direction of alloying [1–4] and in the direction of creating an anode coating from metal alloys [5–8], which form reliable protective oxide films. At the same time, the issues of high-temperature oxidation of metal alloys and intermetallic compounds, especially ways to increase their resistance to oxidation, are the most important aspects of high-temperature oxidation.

Zinc alloys are very widely used in various branches of technology [9–11]. A number of scientific works are devoted to the study of their various properties and industrial operation [12–17]. In addition, the results of a study of the oxidation kinetics of doped zinc-aluminum alloys are presented in [18–20]. There is also information on the oxidation of doped zinc alloys in air [21, 22]. Thus, the effective influence of third elements on the physicochemistry of these alloys has been shown. In this study, attention is paid to the study of the oxidizability of Zn0.5Al zinc alloy doped with neodymium and erbium.

Experimental part

Alloy samples, as objects of study, were obtained in a shaft furnace (SHOL) using metallic zinc (chemically pure), aluminum (A7) and its master alloy containing neodymium (10 % Nd) and erbium

(10 % Er) under a flux layer, a certain composition of NH_4Cl and $ZnCl_2$ (0.1÷0.2 %), in the temperature range 700÷850 °C. Master alloys Al-Nd and Al-Er were preliminarily obtained in a SNVE-1.3.1/16IZ furnace. The resulting master alloys AlNd10 and AlEr10 were separately introduced into the Zn0.5Al zinc alloy melt. The chemical compositions of the alloy samples were subjected to quantitative analysis by weighing their number before and after alloying. When the sample weight and dosage of the alloy samples deviated (>0.5–1 %), the melting was repeated again. Samples (0.01÷1.0 %) of Zn0.5Al+Nd(Er) zinc alloys were accurately cut with a uniform size of 8×4 mm on an EDM machine, carefully polished with sandpaper, and degreased for 10–15 s in a 10 % NaOH solution. Each weighed portion of the alloy sample was taken 1.25g to provide an error in determining the mass change of ±0.5 %. Next, the thermogravimetric method [23–25] was used to study the oxidizability of the Zn0.5Al zinc alloy doped with neodymium and erbium at temperatures of 523–623 K. Then, the resulting oxide film was removed from the surface of the alloy samples and, to obtain information on the composition of the phases, it was studied by X-ray phase analysis [26–28].

Results and discussion

The results of the experimental study of the effect of neodymium and erbium additives on the anodic resistance of the Zn0.5Al hard alloy to high-temperature oxidation are shown in Fig. 1. Curves of the oxidation process of the Zn0.5Al base alloy have a power-law character (Fig. 1a). For the first time in 15 minutes, intense oxidation of the alloys is observed. Then, the kinetics of oxidation slows down during the formation of an oxide pellicle. An inherent feature of the oxidation curves indicates the height of the power-law level. Doping a zinc alloy with neodymium and erbium slightly accelerates

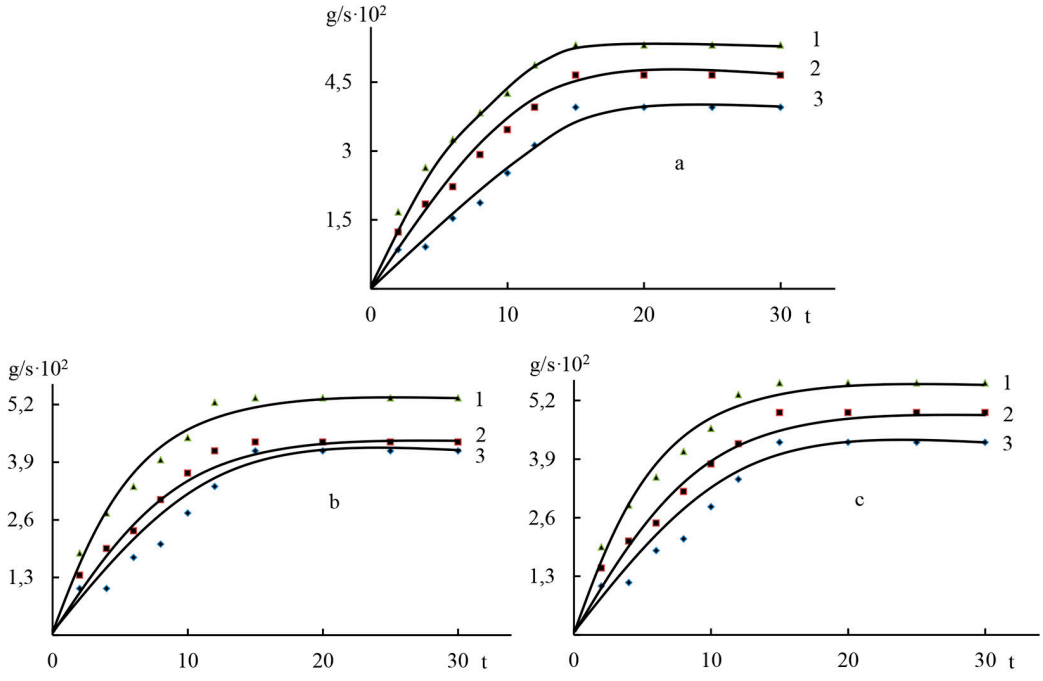

Fig. 1. Kinetic curves (g/s·10², kg/m²) of the oxidation process of Zn0.5Al zinc alloy (a), doped on 0.05 wt% with neodymium (b) and erbium (c), in time (t, min) at T = 623 (1), 573 (2) and 523 (3)

the oxidation kinetics. Zinc alloys alloyed with 0.05 % neodymium and erbium are characterized by a minimum height (g/s) (Fig. 1b, c). The increase in oxide pellicle growth indicates significant formation of pellicle thickness. The addition of more than 0.5 % of neodymium and erbium is impractical, since it significantly increases the oxidizability of the zinc alloy Zn0.5Al. The established kinetic and energy parameters of the oxidation of the studied alloys are summarized in table 1 and 2.

With an increase in temperature, the oxidation rate for all samples of the alloy under study increases. The value of the activation energy of the oxidation process calculated for alloyed alloys with neodymium and erbium (0.5, 1.0 %) indicates some energy costs. An increase in the concentration of neodymium and erbium (more than 0.5 %) in the zinc alloy significantly increases its oxidizability. Doping of the zinc alloy (0.01 and 0.05 % each) with neodymium and erbium contributes to some increase in the true oxidation kinetics. The oxidizability of the Zn0.5Al base alloy proportionally increases with an increase in the content of neodymium and erbium in it. An increase in temperature accompanies an increase in the oxidizability of all the alloys studied. The addition of 1.0 % neodymium and erbium in the composition of the Zn0.5Al zinc alloy is impractical, since it leads to an even greater increase in the oxidation rate. The effective activation energy of the oxidation process of doped zinc alloys with neodymium and erbium changes to decrease (tables 1, 2)

Valuable information about the kinetics of the oxidation of alloys can be obtained by examining the products of their oxidation, that is, the oxide film that forms on the surface of the sample when it is heated. The product of the interaction of oxygen with the metal – oxide forms an oxide film on the

Table 1. Kinetic and energy parameters of the oxidation process of Zn0.5Al zinc alloy, doped with neodymium, in solid state

Content Nd in the alloy, wt%	Temperature of oxidation, K	True oxidation rate $K \cdot 10^4$, $kg \cdot m^{-2} \cdot s^{-1}$	Effective activation energy, kJ/mol
-	523	3.68	168.4
	573	3.91	
	623	4.11	
0.01	523	3.65	165.3
	573	3.96	
	623	4.11	
0.05	523	3.73	160.6
	573	4.04	
	623	4.28	
0.1	523	3.87	157.2
	573	4.16	
	623	4.35	
0.5	523	4.07	152.0
	573	4.50	
	623	4.91	
1.0	523	4.18	145.9
	573	4.67	
	623	5.00	

Table 2. Kinetic and energy parameters of the oxidation process of Zn0.5Al zinc alloy, doped with erbium, in solid state

Content Er in the alloy, wt%	Temperature of oxidation, K	True oxidation rate $K \cdot 10^4$, $kg \cdot m^{-2} \cdot s^{-1}$	Effective activation energy, kJ/mol
-	523	3.68	168.4
	573	3.91	
	623	4.11	
0.01	523	3.75	164.7
	573	4.06	
	623	4.21	
0.05	523	3.83	159.5
	573	4.14	
	623	4.39	
0.1	523	3.98	156.0
	573	4.25	
	623	4.46	
0.5	523	4.18	151.3
	573	4.61	
	623	5.02	
1.0	523	4.29	144.8
	573	4.78	
	623	5.13	

surface of the metal, which reduces its chemical activity. In terms of thickness, films on metals can be thin (up to 40 nm), medium (40–500 nm) and thick (more than 500 nm). Oxide films can be continuous or non-continuous. According to Pilling and Bedworth, the continuity condition is that the molecular volume of the oxide must be greater than the volume of the metal spent on the formation of the oxide molecule, that is, Vok / Vme > 1, otherwise the film is not continuous [27].

The results of the study show that the influence of the third component in the formation of oxidation products depends on the activity of the metal used. Neodymium and erbium are unique metals that are capable of forming protective oxide layers on the surface of the samples of the alloy under study. During the oxidation of these alloys, are formed protective oxides of ZnO, Al_2O_3, Nd_2O_3, Er_2O_3, $ZnAl_2O_4$ (Fig. 2).

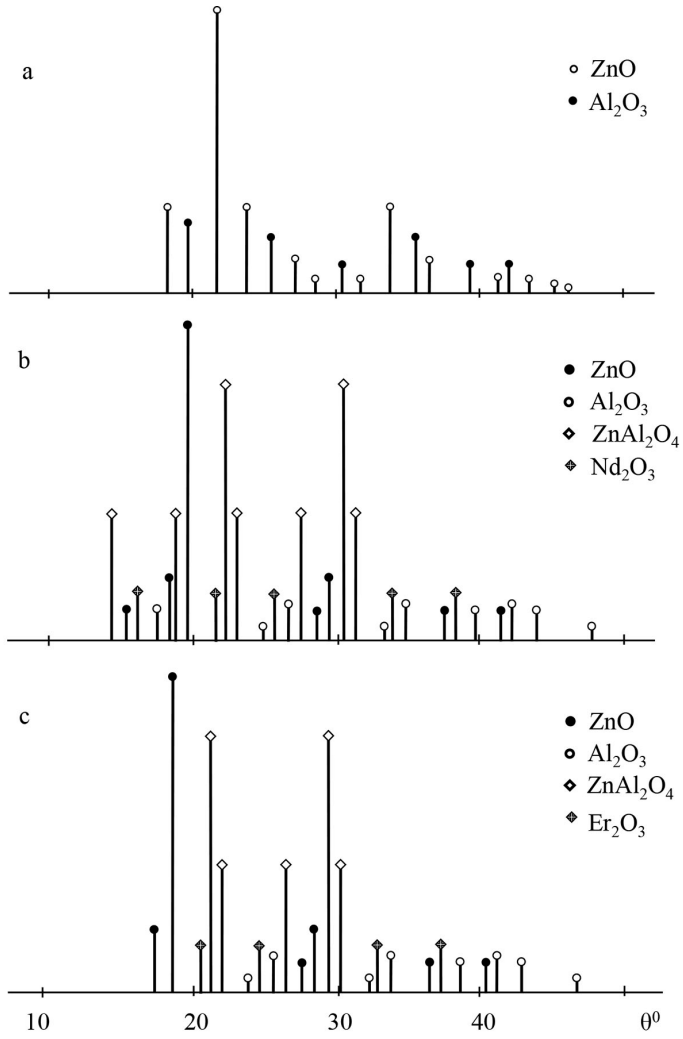

Fig. 2. Bar X-ray patterns of the oxidation products of Zn0.5Al zinc alloy (a) doped with on 0.01 wt% neodymium (b) and erbium (c)

Conclusions

When alloying the zinc alloy Zn0.5Al with neodymium and erbium, showed that the oxidation rate of the alloys somewhat increases with the time of interaction of the alloys with oxygen in the gas phase. Comparison of the oxidation rate of alloys with neodymium and erbium shows that the oxidation rate increases from neodymium to erbium, as evidenced by a decrease in the activation energy.

Thus, the resulting determined that alloys with small additions of neodymium and erbium are characterized by the lowest value of the true oxidation rate. The developed alloys as protective coatings can be recommended for anodic corrosion protection of carbon steel products and structures.

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