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The Influence of Thallium Additives on the Kinetics of Oxidation of the Zn22Al Alloy

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Abstract. The article presents the results of a thermogravimetrical study of the effect of thallium alloying additives on the oxidation kinetics of the Zn22Al alloy. Established in the temperature range of 473–623 K the kinetic and energy parameters of the oxidation of alloys. The oxidation of alloys proceeds according to the hyperbolic mechanism and has the order of 10^{-4} kg·m^{-2}·sec^{-1}. Higher activation energies indicate that the oxidation of these alloy samples results in the formation of oxide films with good protective properties. Additives of thallium in amounts of 0.01–1.0 wt.% contribute to a decrease in the oxidizability of the Zn22Al alloy. The resulting products during the oxidation of the studied alloys consist of a mixture of oxides ZnO, $ZnAl_2O_4$, Al_2O_3, Tl_2O_3.

Keywords: Zn22Al alloy, thallium, thermogravimetrical method, oxidation rate, activation energy.

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Влияние добавок таллия
на кинетику окисления сплава Zn22Al

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Аннотация. В статье приведены результаты термогравиметрического исследования влияния легирующих добавок таллия на кинетику окисления сплава Zn22Al. В интервале температур 473–623 K установлены кинетические и энергетические параметры процесса окисления сплавов. Окисление сплавов протекает по гиперболическому механизму и имеет порядок 10^{-4} кг·м$^{-2}$·сек$^{-1}$. Более высокие значения энергий активации свидетельствуют о том, что при окислении данных образцов сплавов образуются оксидные пленки с хорошими защитными свойствами. Добавки таллия в количествах 0.01–1.0 мас.% способствуют уменьшению окисляемости сплава Zn22Al. Образующиеся продукты при окислении изученных сплавов состоят из смеси оксидов ZnO, $ZnAl_2O_4$, Al_2O_3, Tl_2O_3.

Ключевые слова: сплав Zn22Al, таллий, термогравиметрический метод, скорость окисления, энергия активации.

Introduction

The study of high-temperature oxidation of metals and alloys, in the solid state, in air is of scientific and practical interest. High-temperature oxidation, which is the basis of gas corrosion, is, in turn, a rather complex process that determines the laws of growth of oxide layers. The oxidizing gas, in addition to oxygen, can be sulfur- and carbon-containing gases, etc. The destruction of oxide films, changing the laws of growth, accelerates the high-temperature oxidation of metals and alloys [1–5].

Thus, one of the topical problems of materials science is the preparation of high-temperature corrosion-resistant materials intended for long-term operation under harsh conditions [6–9].

In recent years, there have been works devoted to the experimental study of various properties of Zn-Al alloys for various purposes of operational purposes [10–19]. There are data on the kinetics of the oxidation of these alloys with some metals by atmospheric oxygen [20–25].

The purpose of this work is to study the effect of temperature and thallium dopant on the oxidation kinetics of the Zn22Al alloy.

Experimental part

In this work, the following materials were used: alloy samples were obtained from zinc of the KhCh grade (granulated), aluminum of the A7 grade, and thallium metal of the Tl-OO grade by direct alloying of the components under a protective flux layer of the composition NH4Cl and ZnCl2 (0.1–0.2 % by weight of the charge) in aluminum oxide crucibles in a shaft furnace of the SShOL type in the temperature range of 700–850 °C. The charge was weighed on an analytical balance of the ARV-200 type. Samples with a diameter of 8 mm and a length of 4 mm were prepared on an EDM machine. To

remove the surface layer contaminated with impurities during cutting, the samples were ground with sandpaper and degreased for 10–15 s in a 10 % NaOH solution. The sample weight was 1.25 g, which provides an error in determining the mass change of ±0.5 %.

The kinetics of the oxidation of alloys in the solid state was studied by the thermogravimetrical method. The studies were carried out on a setup [26–28] consisting of a coal resistance furnace with an aluminum oxide casing. The change in the weight of the alloys was recorded by the tension of the spring using a KM-8 cathetometer. At the end of the experiments, the crucible with its contents was weighed and the reaction surface was determined. The resulting oxide film was removed from the sample surface and studied by X-ray phase analysis [29]. The phase analysis of the oxidation products was carried out on a DRON-2.0 diffractometer with copper radiation.

Results and discussion

The obtained kinetic curves testify to the complex character of the alloy oxidation process. The length of time (t) for observing the oxidation kinetics was 1 hour. Due to the fact that the kinetic curves of oxidation from 15 min to 1 hour acquire an unchanged form, the curves only show the course of the process up to 30 min. An inherent feature of the oxidation curves indicates the height of the power-law level (Fig. 1). The curves of the oxidation process of the Zn22Al binary alloy have a power-law character (Fig. 1a). For the first time in 15 min, the oxidation rate increases sharply, which is associated with cracking and a decrease in the protective properties of the oxide layer. The alloy begins to rapidly oxidize, and the specific surface area of the oxidation products increases. The reason for the decrease in the protective properties of the oxide film when the samples are heated is the difference in the volume expansion coefficients of the alloy particles and the oxide shell.

Doping of the Zn22Al alloy with thallium significantly suppresses the deceleration of the oxidation kinetics. An alloy containing 0.1 wt.% thallium is characterized by a minimum height (g/s). At the initial stage, the oxidation process is controlled by processes at the interface and satisfies a linear law. Subsequently, with an increase in temperature (T), the specific mass (g/s) of all samples in time (t) increases, and diffusion of the reagent through the product layer is the limiting factor. The linear dependence is maintained for 12–15 min, then, as the oxide film is formed, the nature of the oxidative process becomes hyperbolic (Fig. 1b-f). The oxidation of alloys obeys a hyperbolic dependence, which is seen from the quadratic curves (g/s) 2-t, which do not fit straight lines (Fig. 2), as well as from analytical dependences, where the degree of x varies from 2 to 4 (Table 1).

The introduction of 0.01–1.0 % thallium into the Zn22Al alloy improves its resistance to oxidation. The true oxidation rate for an alloy with 0.01 % molybdenum varies from 3.56 to $2.24 \cdot 10{-}4$ kg/(m2·s) at a temperature of 523 K. A change in the composition of the alloy also affects the activation energies. The values of the activation energy obtained by us for the Zn22Al alloy (Table 2) agree satisfactorily with the data of [7]. Thus, the oxidation of alloys with a thallium content of 0.01–0.1 % requires large energy expenditures, and the maximum values of the effective activation energy are 176.4–178.3 kJ/mol (Table 1).

Higher activation energies indicate that the oxidation of these alloy samples results in the formation of oxide films with good protective properties. In the kinetics of oxidation reactions, an important role is played by the initial state (dispersity) and the phase composition of the samples. An increase in the fineness of the alloys leads to an increase in their reactivity, which is clearly manifested
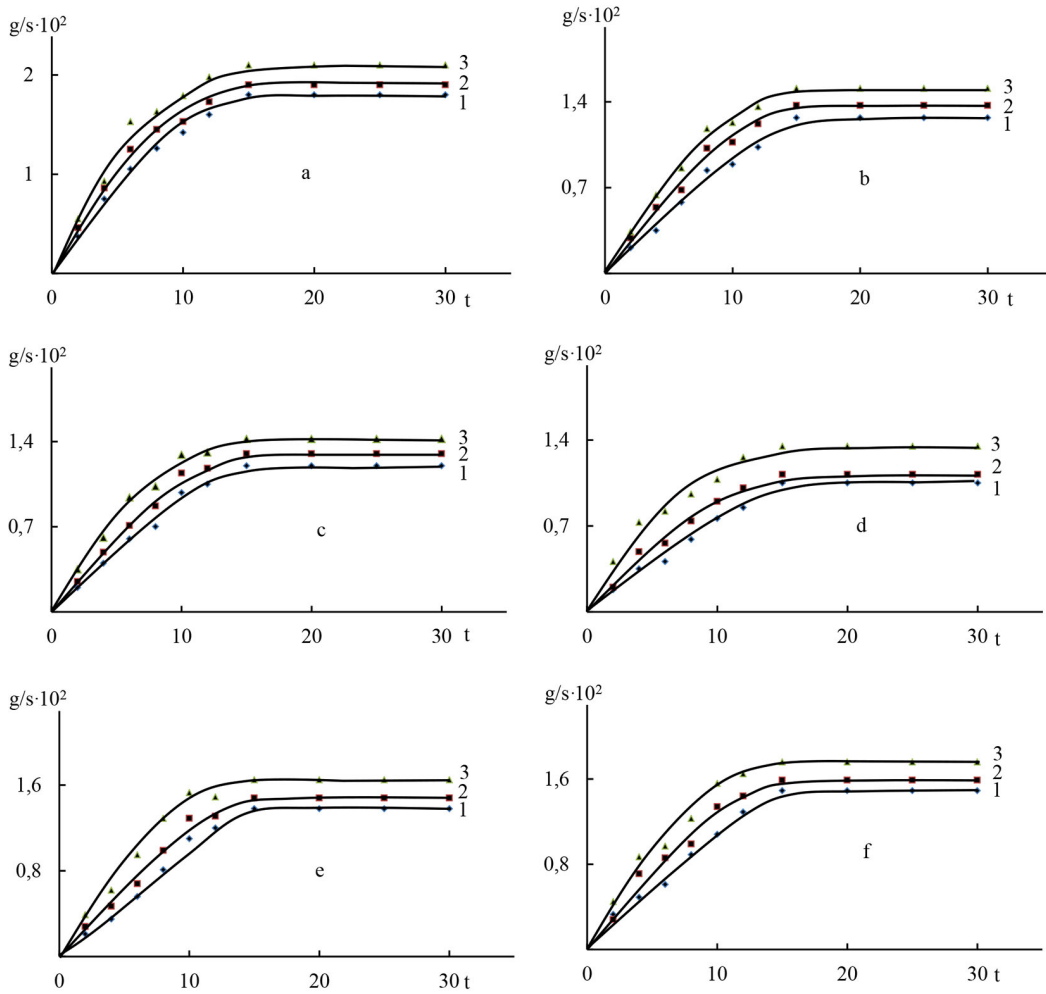
Fig. 1. Kinetic curves (g/s·10^2, kg/m²) of the oxidation process of Zn22Al alloy (a), doped with thallium on wt%: 0.01 (b), 0.05 (c), 0.1 (d), 0.5 (e), 1.0 (f) in time (t, min) at T = 473 (1), 523 (2) and 623 (3)
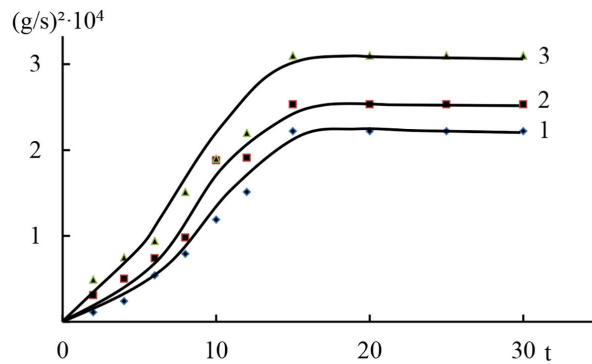
Fig. 2. Quadratic curves for the oxidation of the Zn22Al alloy with 1.0 wt% thallium

Table 1. Results of mathematical processing of the kinetic curves of the oxidation process of the Zn22Al alloy doped with thallium

Content Tl in the alloy, wt%	Temperature of oxidation, K	Polynomials of Alloy Oxidation Curves $(y = Kt^n)$	Approximation confidence level, R
-	473	$y = 0.002t^4 + 0.002t^3 - 0.049t^2 + 0.323t$	0.988
	523	$y = 0.002t^4 + 0.003t^3 - 0.053t^2 + 0.357t$	0.990
	623	$y = 0.003t^4 + 0.005t^3 - 0.069t^2 + 0.615t$	0.993
0.01	473	$y = 0.001t^4 + 0.002t^3 - 0.027t^2 + 0.161t$	0.993
	523	$y = 0.001t^4 + 0.002t^3 - 0.040t^2 + 0.182t$	0.991
	623	$y = 0.002t^4 + 0.003t^3 - 0.048t^2 + 0.202t$	0.995
0.05	473	$y = 0.001t^4 + 0.002t^3 - 0.019t^2 + 0.126t$	0.994
	523	$y = 0.001t^4 + 0.002t^3 - 0.034t^2 + 0.149t$	0.992
	623	$y = 0.002t^4 + 0.003t^3 - 0.041t^2 + 0.185t$	0.996
0.1	473	$y = 0.001t^4 + 0.001t^3 - 0.017t^2 + 0.117t$	0.992
	523	$y = 0.001t^4 + 0.002t^3 - 0.046t^2 + 0.136t$	0.994
	623	$y = 0.002t^4 + 0.003t^3 - 0.037t^2 + 0.178t$	0.993
0.5	473	$y = 0.001t^4 + 0.002t^3 - 0.032t^2 + 0.174t$	0.993
	523	$y = 0.002t^4 + 0.003t^3 - 0.050t^2 + 0.189t$	0.990
	623	$y = 0.002t^4 + 0.003t^3 - 0.054t^2 + 0.212t$	0.990
1.0	473	$y = 0.001t^4 + 0.002t^3 - 0.038t^2 + 0.182t$	0.992
	523	$y = 0.002t^4 + 0.003t^3 - 0.083t^2 + 0.195t$	0.991
	623	$y = 0.002t^4 + 0.004t^3 - 0.097t^2 + 0.221t$	0.991

Table 2. Kinetic and energy parameters of the oxidation process of Zn22Al alloy, doped with thallium, in solid state

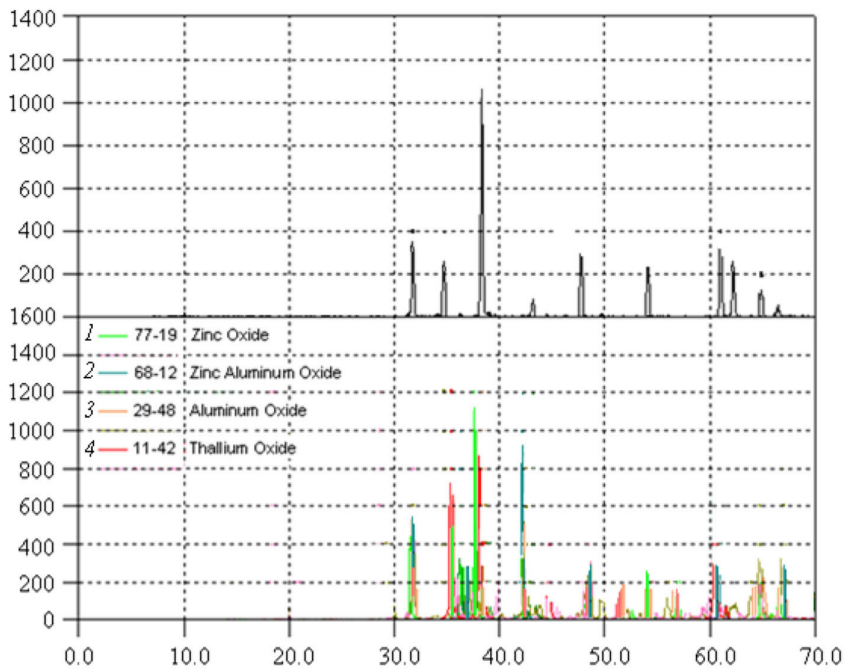| Content Tl in the alloy, wt%	Temperature of oxidation, K	True oxidation rate $K \cdot 10^4$, kg·m^{-2}·s^{-1}	Effective activation energy, kJ/mol
-	473	3.12	
	523	3.56	151.2
	623	3.91	
0.01	473	2.18	
	523	2.48	176.4
	623	2.73	
0.05	473	2.11	
	523	2.40	177.6
	623	2.66	
0.1	473	2.05	
	523	2.24	178.3
	623	2.56	
0.5	473	2.21	
	523	2.57	174.5
	623	2.84	
1.0	473	2.41	
	523	2.81	171.8
	623	3.00	

Fig. 3. X-ray diffraction patterns of the oxidation products of Zn22Al alloy with 0.01 wt% thallium

in an increase in the temperatures of the onset of oxidation and in the values of the effective activation energy. The higher temperature interval for the onset of sample oxidation is due to the fact that the oxidation process is accompanied by the formation of an oxide film, the thickness of which is much smaller than the sample dimensions. Higher values of the effective activation energy for ternary alloys are explained by the formation of aluminates of complex composition on their surface, which are chemically quite stable.

Thus, valuable information on the kinetics of oxidation of alloys can be obtained by studying 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 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). Oxides of the spinel type $Me'O \cdot Me''_2O_3$ ($Me'Me''_2O_4$) have a higher protective ability than oxides of each metal separately [28].

As a result of the oxidation of hard alloys, according to X-ray diffraction analysis, oxides ZnO (1), $ZnAl_2O_4$ (2), Al_2O_3 (3), Tl_2O_3 (4) (Fig. 3), aluminates and spinels of complex composition are formed, and there are crystalline phases of the initial components.

Conclusions

As a result of an experimental study, a hyperbolic mechanism for the oxidation of Zn22Al-Tl alloys was established. The kinetic and diffusion regimes of the oxidation of alloys by atmospheric oxygen are revealed. Showed the possibility of increasing the anodic resistance of the Zn22Al alloy to oxidation by doping with thallium (0.01–1.0 %).

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