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Kinetics of Oxidation of Lithium-Modified Lead–Antimony Alloy SSu3 in the Solid State

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Abstract—The oxidation of the lead alloy SSu3 with lithium in air under isothermal conditions was studied by thermogravimetry while continuously recording the sample mass for 1 h at temperatures of 473, 523, and 573 K. Kinetic curves of oxidation of the SSu3 alloy with lithium were constructed based on the experimental data. The dependences of the specific weight increment on the amount of the alloying additive and temperature were determined from the curves. A lithium addition of up to 1.0 wt % increases the rate of oxidation of the lead alloy, which is accompanied by a decrease in the apparent activation energy of oxidation. Quadratic kinetic curves of alloy oxidation were constructed. The mechanism of oxidation of alloys was established.

The oxidation of alloys in the given temperature range of 473–573 K obeys the hyperbolic law $y = kx^n$, where $n = 1–4$.

Keywords: lead alloy SSu3, lithium, thermogravimetric method, oxidation kinetics, true oxidation rate, apparent activation energy

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INTRODUCTION

The solution to many problems in modern technology involves the use of materials with high oxidation resistance. The study of the interaction of oxygen with metals and alloys acquired great importance due to their wide use in various fields of science and technology. There is no information in the literature on the heat resistance of lead alloys doped with lithium.

Lead is the fifth metal most widely used in the world. The most important applications of lead and its alloys are lead-acid batteries (in grid plates, posts, and bonding tapes), ammunition, cable sheath, and construction materials (such as sheets, pipes, solder, etc.). Other important areas of their application are counterweights, battery clamps, and other cast products (bearings, gaskets, cast metal, and foil) [1].

Lead in various forms and combinations is increasingly used as a material for suppressing sound and mechanical vibrations. It is also important in many forms as protection against X-rays and gamma rays (in nuclear industry). In addition, lead is used as an alloying element in steel and copper alloys to improve workability and other characteristics, and also in low-melting alloys for fire sprinklers in fire-fighting systems [2–4].

Lead-based alloys are very promising for creating new materials. For effective operation of such materials at high temperatures, it is necessary to know the kinetic parameters of oxidation, which make it possible to determine the most optimum temperature conditions for each alloy. This information is extremely scanty in the literature [5, 6]. There is information about the positive effect of alkali metals on the corrosion resistance of lead babbits [7–9]. It was also reported that corrosion resistance of lead and its alloys is increased by doping with lithium [10, 11]. Our work [12] reported a 20% increase in the anodic stability of the initial SSu3 alloy when alloyed with lithium.

The purpose of this work was to study the effect of lithium addition on the oxidation kinetics of a lead–antimony alloy (SSu3) in the solid state. To solve the problem, the thermogravimetry method with continuous weighing of samples was used.

EXPERIMENTAL

The kinetics of alloy oxidation was studied under nonisothermal conditions in an air atmosphere using the method described in [13–17]. A diagram of the unit for studying the kinetics of alloy oxidation is shown in Fig. 1. The main parts of the unit are the Tammann furnace (*1*) and its alumina case (*2*). In the experiments, the case in the upper part was closed with water-cooling covers (*7*). The covers had holes for the gas-conducting tube (*3*), crucible (*4*) for alloy samples, and thermocouples (*5*). The sample was suspended on a platinum thread (*6*) to a spring. The

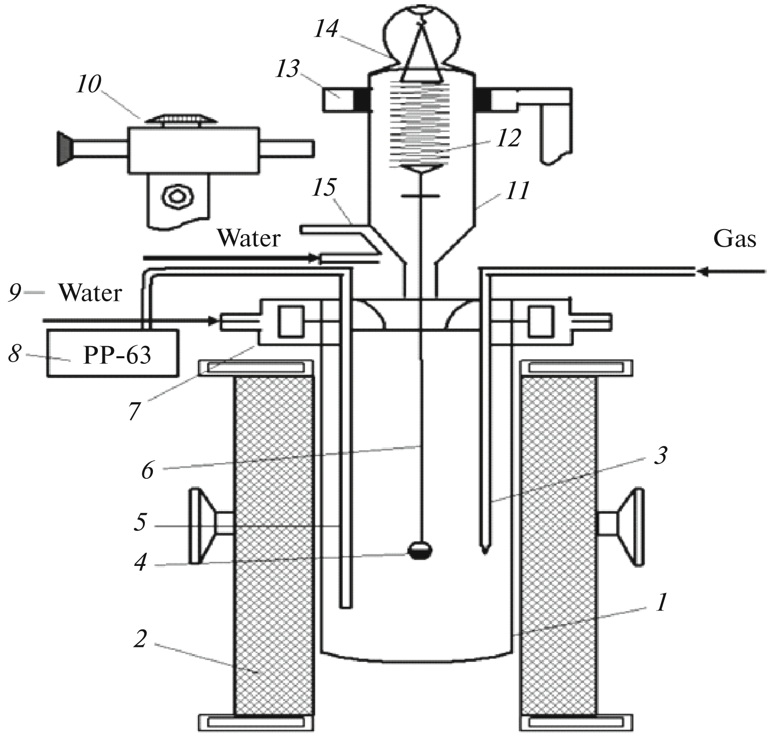

Fig. 1. Diagram of the unit for studying the kinetics of oxidation of metals and alloys: (*1*) Tammann oven, (*2*) alumina case, (*3*) gas-conducting tube, (*4*) crucible, (*5*) thermocouple, (*6*) platinum thread, (*7*) water-cooled cover, (*8*) potentiometer, (*9*) water, (*10*) cathetometer, (*11*) molybdenum glass case, (*12*) molybdenum wire spring, (*13*) stand, (*14*) cap, (*15*) refrigerator chair.

spring (*12*) was made of molybdenum wire. The spring was preliminarily calibrated and inserted into a molybdenum glass cylinder (*11*) with a ground-in stopper (*14*). The case with the spring was fixed on a stand (*13*) that was independent of the furnace to eliminate vibrations and shocks. To protect the scales from heat radiation of the furnace, a cooler chair (*15*) was used at the lower end of the cylinder.

The change in the mass of the sample was recorded based on spring extension using a KM-8 cathetometer. In our experiments, we used alumina crucibles with a diameter of 18–20 mm and a height of 25–26 mm. Before the experiment, the crucibles were calcinated to a constant weight at 1273–1473 K in an oxidizing atmosphere for 1.5 h. The alloys in the solid state were oxidized in air at constant temperatures of 473, 523, and 573 K. The crucible with the test sample was placed in the isothermal zone of the furnace. The metal was heated in an air atmosphere. The temperature was raised at a rate of 2–3°C/min. Before heating the furnace, the cathetometer was adjusted to the spring indicator, the reference point was recorded on the scale, and the change in the mass was monitored during heating. When the specified mode was reached, a new reference point was recorded.

The average rate of oxidation of the alloys was determined from the tangents drawn through the majority of the experimental points to the oxidation curves of the alloys.

The results of the thermogravimetric study of the oxidation kinetics of the lithium-doped SSu3 lead alloy are given in Table 1. It was established that the average rate of oxidation of the initial alloy increases depending on the composition and temperature of the alloys under study at additive concentrations from 0.05 to 1.0 wt % lithium. Thus, the average rate of oxidation is 2.50×10^{-4}–3.25×10^{-4} kg m^{-2} s^{-1} for the initial alloy in the temperature range 473–573 K and 2.65×10^{-4}–3.40×10^{-4} kg m^{-2} s^{-1} for the alloy with a 1.0 wt % lithium addition at the same temperatures. The effective activation energy of oxidation for the above alloys decreases from 38.32 to 30.10 kJ/mol, respectively. The kinetic and energy parameters of the oxidation of alloys are determined by the structure of the resulting oxide films. If the oxide film formed on the samples is loose, the oxygen transfer through it is facilitated and the oxidation rate accordingly increases. The formation of a dense film hinders the oxygen transport through it, leading to a decrease in the process rate.

As an example, Fig. 2 presents the kinetic curves of oxidation, which characterize the change in the mass over time for the lead alloy SSu3 containing 0.05–

Table 1. Kinetic parameters of oxidation of the SSu3 alloy with lithium in the solid state

[Li], wt %	T, K	$K \times 10^4$, kg m^{-2} s^{-1}	Q, kJ/mol
0.0	473 523 573	2.50 2.77 3.25	38.32
0.05	473 523 573	2.53 2.80 3.28	37.01
0.1	473 523 573	2.57 2.85 3.32	35.50
0.5	473 523 573	2.61 2.89 3.36	32.90
1.0	473 523 573	2.65 2.94 3.40	30.10

[Li] is the lithium content in the alloy; T, oxidation temperature; K, average oxidation rate; Q, apparent activation energy of oxidation; and g/s, specific weight increment of the samples.

1.0 wt % lithium at 473, 523, and 573 K. The oxidation occurs with diffusion hindrances and ends in 15–20 min.

The quadratic kinetic curves of oxidation of the SSu3 alloy with lithium (0.05–1.0 wt %) are presented in Fig. 3.

The results of the mathematical processing of the quadratic kinetic curves of alloy oxidation in the $(g/s)^2$–t coordinates are summarized in Table 2. The polynomials of the alloy oxidation curves indicate that the oxidation is described by the hyperbolic equation $y = kx^n$, where $n = 1$–4.

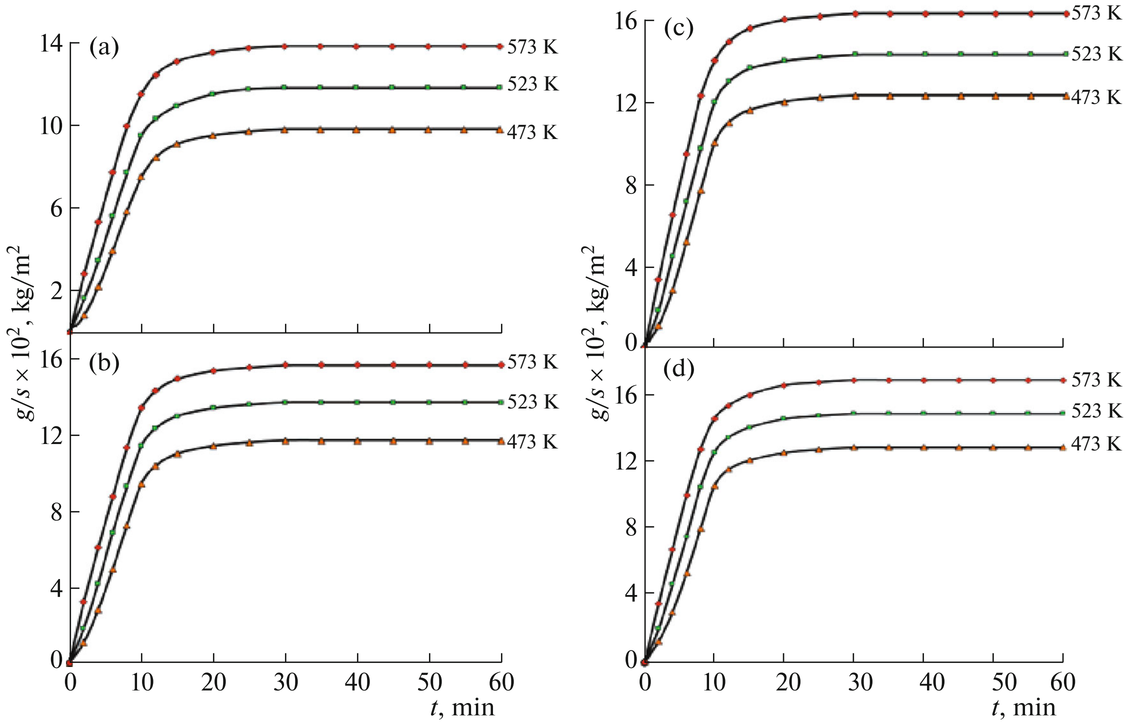

Fig. 2. Kinetic curves of oxidation of the (a) SSu3 alloy and the alloy with (b) 0.1, (c) 0.5, and (d) 1.0 wt % lithium.

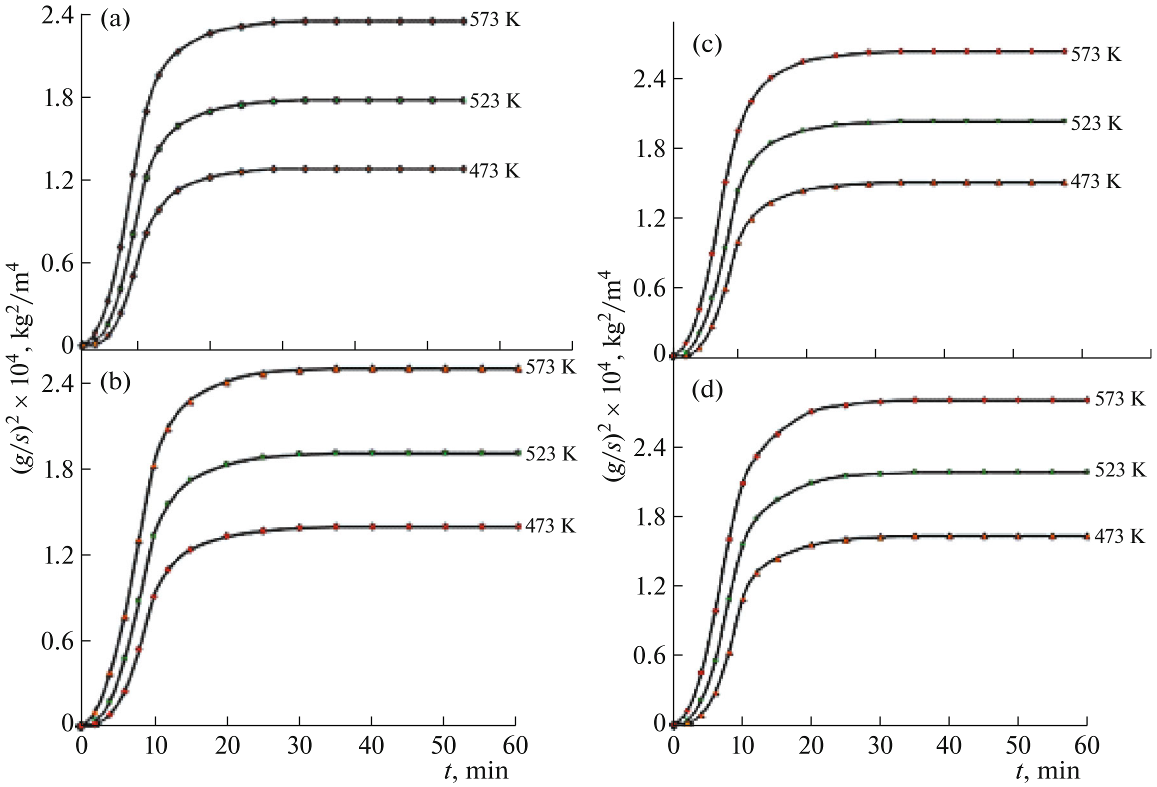

Fig. 3. Quadratic curves of oxidation of the (a) SSu3 alloy and the alloy with (b) 0.1, (c) 0.5, and (d) 1.0 wt % lithium.

The isochrones of oxidation of the alloys corresponding to the temperatures of 473 and 573 K are shown in Fig. 4. The lines show a tendency for the oxidation rate of the initial alloy to increase as the lithium content increases to 1.0 wt %, which is accompanied by a decrease in the apparent activation energy of oxidation.

Table 2. Polynomials of the quadratic kinetic curves of oxidation of the SSu3 alloy with lithium in the solid state

[Li], wt %	T, K	Polynomials of quadratic kinetic curves of alloy oxidation	R^2
0.0	473	$y = -0.6 \times 10^{-4}x^4 + 0.7 \times 10^{-3}x^3 - 0.045x^2 + 1.2074x$	0.977
	523	$y = -0.6 \times 10^{-6}x^4 + 0.1 \times 10^{-3}x^3 - 0.0596x^2 + 1.4699x$	0.988
	573	$y = -0.6 \times 10^{-9}x^4 + 1.5 \times 10^{-3}x^3 - 0.0792x^2 + 1.7884x$	0.995
0.05	473	$y = -0.6 \times 10^{-3}x^4 + 0.6 \times 10^{-3}x^3 - 0.042x^2 + 1.1729x$	0.975
	523	$y = -0.6 \times 10^{-6}x^4 + 0.1 \times 10^{-3}x^3 - 0.0607x^2 + 1.5215x$	0.984
	573	$y = -0.5 \times 10^{-1}x^4 + 1.5 \times 10^{-3}x^3 - 0.0843x^2 + 1.9264x$	0.993
0.1	473	$y = -0.6 \times 10^{-3}x^4 + 0.7 \times 10^{-3}x^3 - 0.0442x^2 + 1.2303x$	0.974
	523	$y = -0.6 \times 10^{-7}x^4 + 1.1 \times 10^{-3}x^3 - 0.0648x^2 + 1.6015x$	0.985
	573	$y = -0.5 \times 10^{-1}x^4 + 1.6 \times 10^{-3}x^3 - 0.0884x^2 + 2.0065x$	0.994
0.5	473	$y = -0.6 \times 10^{-4}x^4 + 0.7 \times 10^{-3}x^3 - 0.0466x^2 + 1.2915x$	0.972
	523	$y = -0.6 \times 10^{-7}x^4 + 1.2 \times 10^{-3}x^3 - 0.0678x^2 + 1.6689x$	0.984
	573	$y = -0.5 \times 10^{-1}x^4 + 1.8 \times 10^{-3}x^3 - 0.0953x^2 + 2.1208x$	0.993
1.0	473	$y = -0.6 \times 10^{-4}x^4 + 0.7 \times 10^{-3}x^3 - 0.0486x^2 + 1.3453x$	0.971
	523	$y = -0.6 \times 10^{-8}x^4 + 1.2 \times 10^{-3}x^3 - 0.0722x^2 + 1.7506x$	0.984
	573	$y = -0.5 \times 10^{-1}x^4 + 1.9 \times 10^{-3}x^3 - 0.0991x^2 + 2.1944x$	0.993

R^2 is the regression coefficient; y, specific weight increment of the samples, kg/m^2; x, sample oxidation time, min.

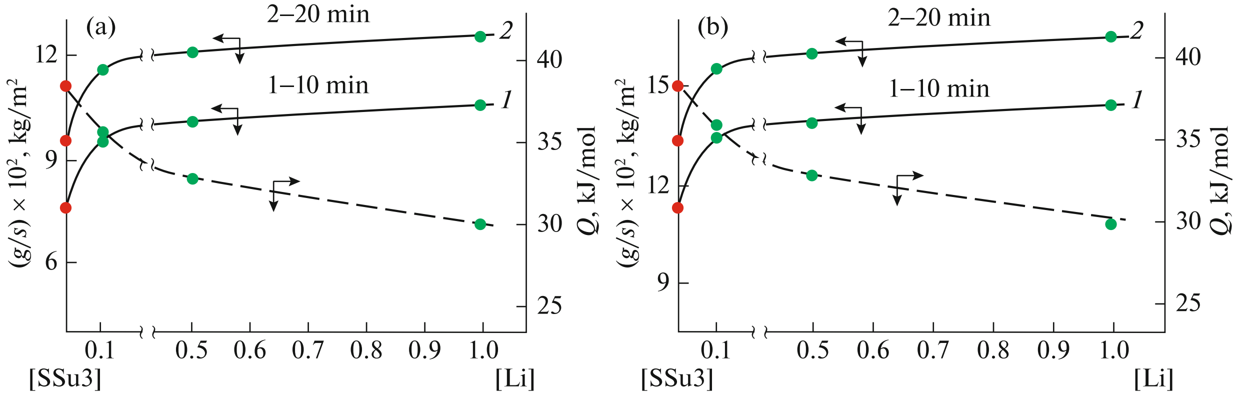

Fig. 4. Isochrones of the oxidation of the SSu3 alloy with lithium at (a) 473 and (b) 573 K (b).

Figure 5 shows the dependences $-\log K - 1/T$ for the SSu3 alloy with lithium. It can be seen that, in general, in the $-\log K - 1/T$ coordinates the curves are linear, and the lines related to alloys with lithium lie above the line for the initial SSu3 alloy. The activation energy of the alloys was determined from the slope of these curves.

The lithium-doped alloys are characterized by a higher true oxidation rate compared to the initial SSu3 alloy of lead and antimony. This would be expected, since the total rate of oxidation includes a number of stages that are different in nature. We can trace some tendencies characteristic of the oxidation of alloys of this system in the solid state. First of all, the rate of oxidation of alloys increases with temperature. The addition of lithium reduces the apparent activation energy of the oxidation the SSu3 alloy in the solid state. The true oxidation rate constants of the SSu3 alloy with 0.05–1.0 wt % lithium at the same temperatures are slightly higher than the constant of the initial SSu3 alloy. The oxidation rate of the alloys generally increases with increasing temperature and lithium content in the SSu3 alloy.

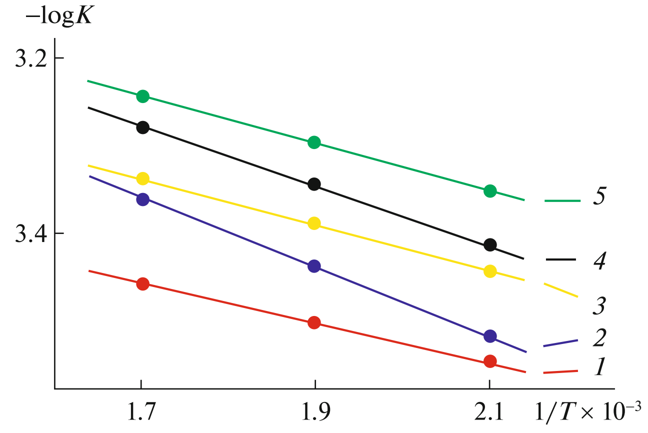

Fig. 5. Dependences of $-\log K$ on $1/T$ for (*1*) lead alloy with antimony SSu3 and for alloys with lithium contents of (*2*) 0.05, (*3*) 0.1, (*4*) 0.5, and (*5*) 1.0 wt %.

The products formed during the oxidation of lithium-doped lead alloy SSu3 were studied by X-ray diffractometry on a DRON-3M instrument (Fig. 6). According to Fig. 6, the oxidation products are oxides Li_2PbO_3, Pb_3O_4, Sb_2O_3 for the 1 wt % lithium-doped alloy and $PbSb_2O_6$, Sb_2O_4, PbO, Sb_5O_{13} for the initial SSu3 alloy.

The microstructures of the alloys were studied using a BIOMED-1 microscope. Figure 7 presents the microstructures of the samples before and after modification with lithium. It can be seen that lithium additives, especially 0.1 wt % Li, lead to significantly reduced structural components of the initial SSu3 alloy.

CONCLUSIONS

Many problems in modern technology are solved using materials with high oxidation resistance. In particular, doping processes play a significant role in creating new corrosion-resistant materials and improving the corrosion characteristics of existing materials. In view of their exceptional importance, data on the behavior of metals and alloys in oxidizing media evidently need to be completely systematized. This paper presents the experimental results relating to the behavior of the lead–antimony alloy SSu3 in a gas atmosphere at high temperatures. Studies of the influence of lithium on the oxidation of the SSu3 alloy show that doping with up to 1.0 wt % lithium enhances the oxidation of the initial alloy via the mechanism of formation of multicomponent oxides of the spinel type, which do not have sufficient protective properties. As small concentrations of lithium in the SSu3 alloy slightly enhance the oxidation of alloys, these concentrations can be considered appropriate for the operation of products made from these alloys at low temperatures.

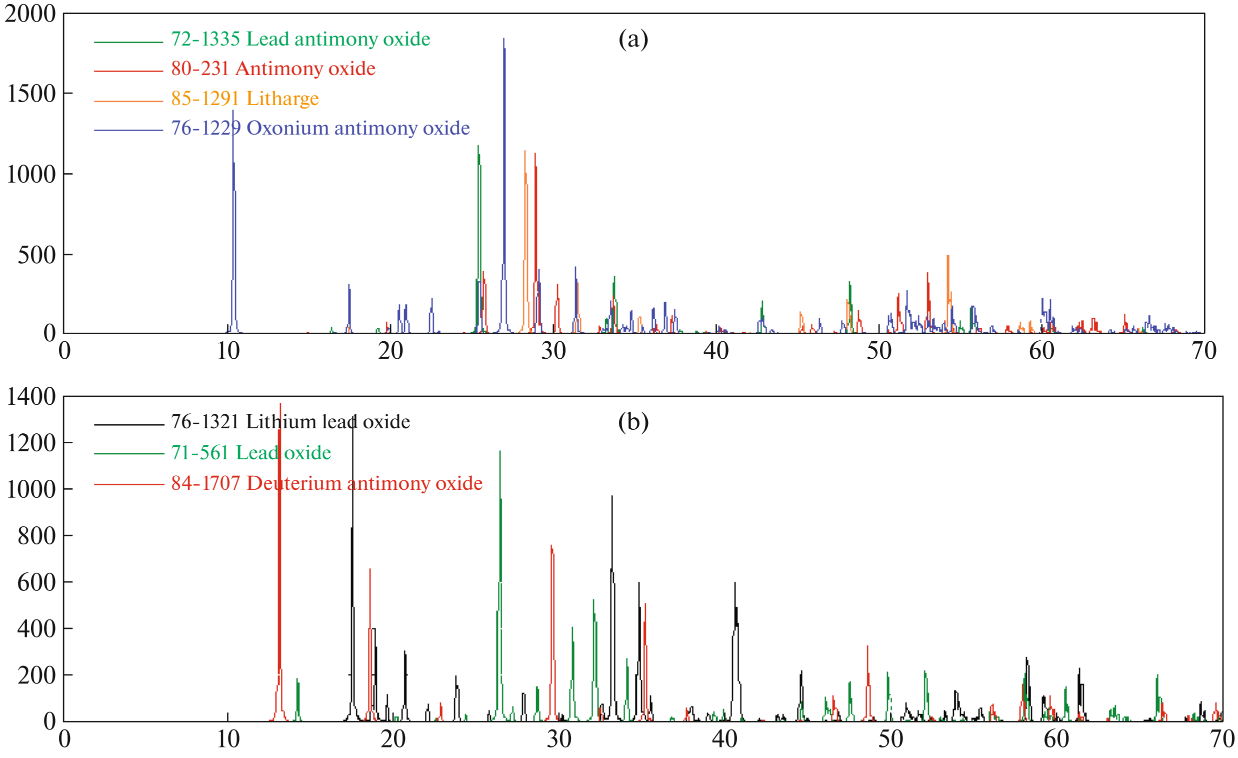

Fig. 6. Bar diagrams of the oxidation products of the (a) SSu3 alloy and (b) the alloy with 1.0 wt % lithium.

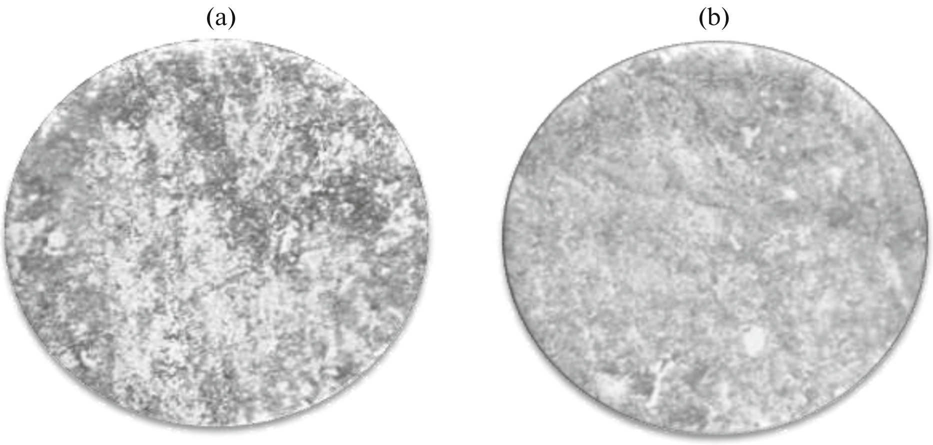

Fig. 7. Microstructures (×500) of the (a) SSu3 alloy and (b) alloy containing 0.1 wt % lithium.

Thus, the dependence of the oxidation rate of the SSu3 alloy on the lithium content and temperature was studied using thermogravimetry. It was shown that the oxidation rate of SSu3 increases with the temperature and lithium concentration. Polynomials of the quadratic kinetic curves of alloy oxidation were obtained, and using these polynomials it was established that oxidation proceeds by a hyperbolic mechanism.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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