

In Situ Investigation of Oxidation of Aluminum Alloy Powders with Calcium and Barium by Synchrotron Radiation

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Abstract The phase composition and structure of initial powders and the products of oxidation of aluminum alloys with calcium and barium containing 0.88 and 0.26 at.% of dopants, respectively, have been studied for the first time by the diffraction method with the use of synchrotron radiation during programmed heating in air up to 1273 K at a rate of 10 K/min. It was established that as a result of the heterogeneity of the phase composition of the oxidation products and the structural changes in the oxide shell on the particle surface, aluminum oxide loses its high protective properties and metal oxidation is activated.

Keywords Aluminum Powders, Completeness of Oxidation, Alloying, In Situ Study of Structural Transformation

additive, which is present there in the structure of ordered microgroups corresponding to the most stable intermetallics, as shown in [4].

In [5], it was found that the intermetallic compounds in the structure of aluminum-based alloys play a leading role in the oxidation of powders, since they have higher reactivity with respect to atmospheric oxygen than aluminum.

Unfortunately, the traditional methods of analysis of the products formed during programmed heating in air do not allow one to track the kinetics and sequence of phase formation directly during the interaction [4]. That is why it is interesting to follow these processes in situ by the diffraction method with the use of synchrotron radiation, as shown in the works carried out in ISSCM SB RAS to study fast processes [6, 7].

In this work we studied experimentally the physical and chemical processes occurring during oxidation of aluminum-based powders doped with Ca and Ba in air.

1. Introduction

Analysis of the physicochemical properties of aluminum-based alloys and the experimental data on their oxidation during programmed heating showed that structure heterogeneity of the metal core of the powders and the products of interaction on the surface contributes to the discontinuity of the barrier layer and increases the reactivity [1]. High segregation of Ca and Ba in the surface layers of aluminum-based alloy powders was established by XPS [2, 3].

Based on the results of these studies it was suggested that calcium and barium concentrate on the particle surface in the form of intermetallic compounds corresponding to aluminum-richest compositions (Al_4Ca , Al_4Ba) on the phase diagrams of the investigated binary systems. The greatest influence on the heterogeneity of oxidation products on the surface of particles is exerted by surface-active metals. Concentrating in the surface layers, they activate the oxidation process. When the alloys transform into liquid state, the particle surface is enriched with a surface-active

2. Experimental Section

The examined powders of aluminum-based alloys with calcium and barium were obtained by spraying the melt with nitrogen. The metal content was ~99%. The specific surface area was measured on a Tristar 3000 v. 6.03 A device by thermal desorption of argon and amounted to 0.47 m²/g for spherically-shaped particles, which corresponds to the average particle diameter of about 5 microns. The content of calcium and barium in the powders was determined by mass spectrometry with inductively coupled plasma on an ELAN 9000 instrument to be 0.88 and 0.26 at.%, respectively. The morphology of the particles was analyzed by means of a scanning Electron microscope JSM-6390 JEOL LA. In this work, we used the data of thermogravimetric studies of oxidation of powders in air obtained on a NETZSCH STA 409 PC/PE facility at a heating rate of 10 K/min. [2, 3].

The in situ studies of oxidation of the samples were carried out by X-ray diffraction using synchrotron radiation from the

VEPP-3 station of Channel 4 on the basis of equipment available at ISSCM SB RAS [8].

Monochromatic radiation ($\lambda = 0.308 \text{ \AA}$) passes through a thin layer of the sample and provides a diffraction pattern recorded by a flat two-dimensional detector. The detector is a system based on storage screens MAR345 (Marresearch). The powder sample was placed into the hole of the aluminum oxide holder and heated in air at a rate of 10 K/min up to 1273 K [8].

Results and Discussion

As a result of diffraction studies (Figure 1a) with the use of

synchrotron radiation, it can be stated that the initial phase composition of the Al-Ca alloy includes Al, Al_2O_3 , Al_2Ca and Al_4Ca . This pattern persists up to the melting point, where the peaks are only displaced owing to an increase in the lattice parameters induced by thermal expansion. In case of the Al-Ba alloy, the initial phase composition (Al, Al_4Ba , Al_2O_3) remains up to the eutectic melting point (923 K) (Figure 1b).

The amount of intermetallics found in the structure of the alloy powders is consistent with the equilibrium phase diagrams of the alloys Al-Ca, Ba [9].

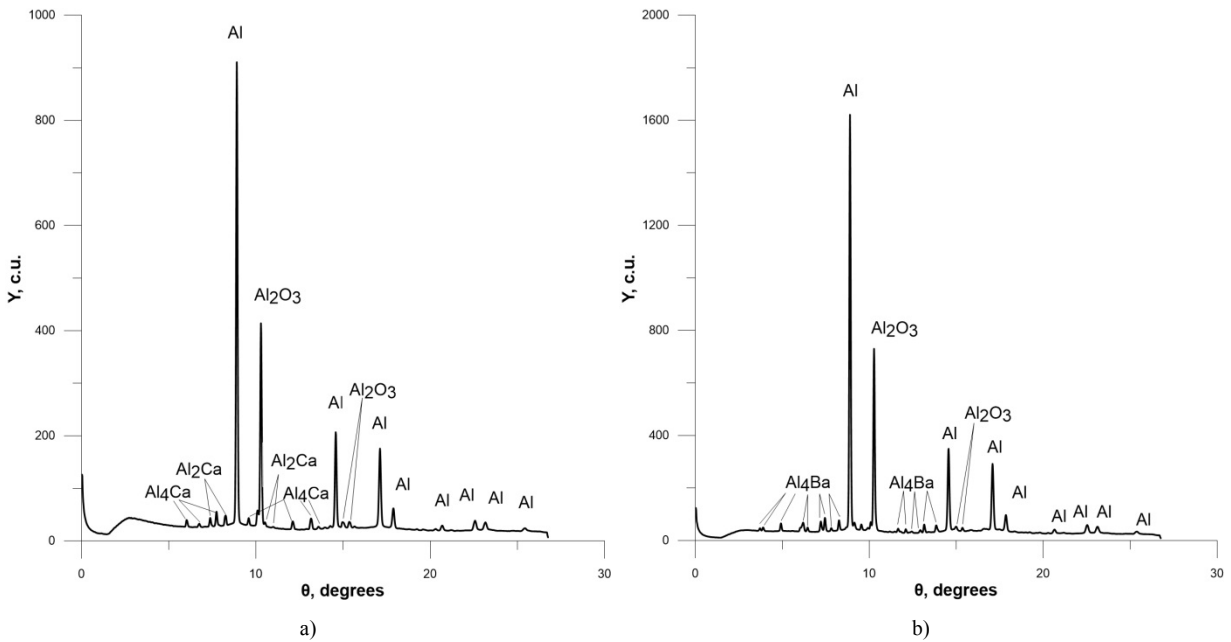


Figure 1. The X-ray diffraction patterns of the alloy powder at 773 K: a) Al-Ca; b) Al-Ba.

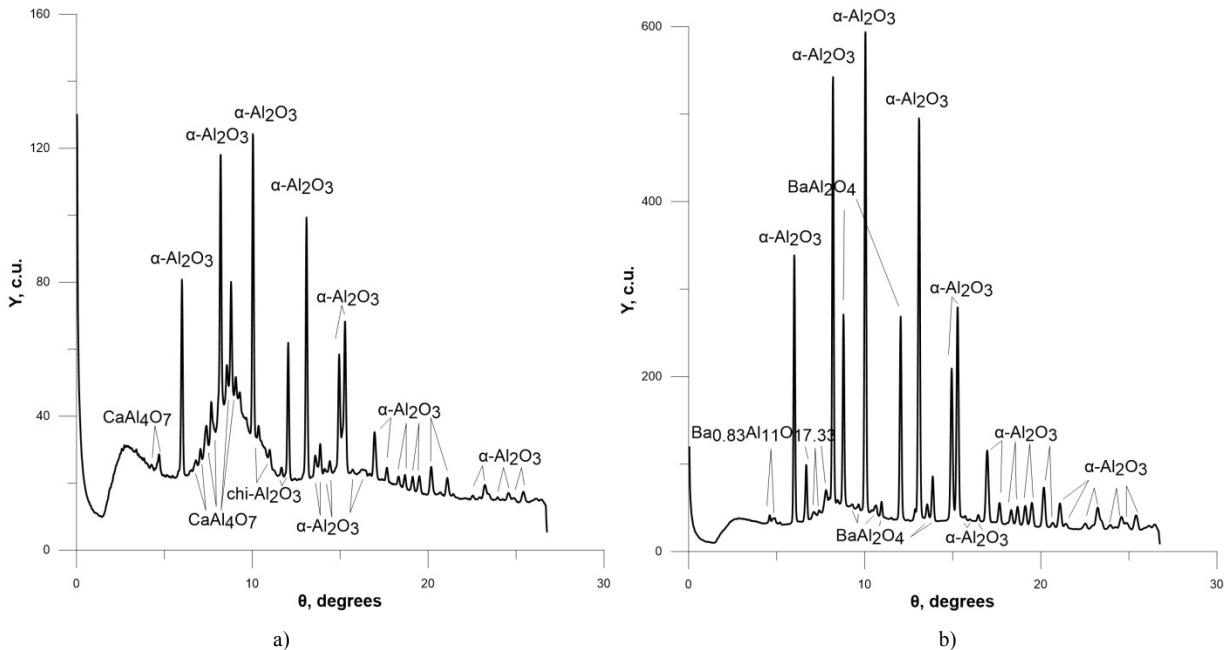


Figure 2. The X-ray diffraction patterns of the alloy powder at 1273 K: a) Al-Ca; b) Al-Ba.

After melting, the peaks of aluminum and intermetallics in the aluminum alloys with calcium disappear. Intensity maxima corresponding to CaAl_4O_7 and Al_2O_3 emerge. At 1273 K, two modifications of alumina ($\alpha\text{-Al}_2\text{O}_3$ and $\chi\text{-Al}_2\text{O}_3$) and the double oxide CaAl_4O_7 are found in the Al-Ca system (Figure 2a).

Upon the heating of the Al-Ba powder above the melting temperature, Al_4Ba remains, and at further heating, in case of oxidation, two double oxides, BaAl_2O_4 and $\text{Ba}_{0.83}\text{Al}_{11}\text{O}_{17.33}$, are formed and aluminum oxide is present in the form of $\alpha\text{-Al}_2\text{O}_3$ (Figure 2b).

The results of the thermogravimetric studies of the Al-Ca

alloy powder (Figure 3) show [2] that the completeness of oxidation of the calcium alloy powder in the temperature range 1300-1550 K is at least twice as large as that of pure aluminum. Even at the maximum heating temperature, 1750 K, the completeness of oxidation of the alloy powder is 1.65 times higher.

Comparison of the obtained results shows that the presence of four phases (alumina, two aluminum intermetallics and aluminum) in the structure of the initial alloy particles significantly changes the aluminum oxidation pattern. Beginning with 1000 K, the oxidation process becomes very active.

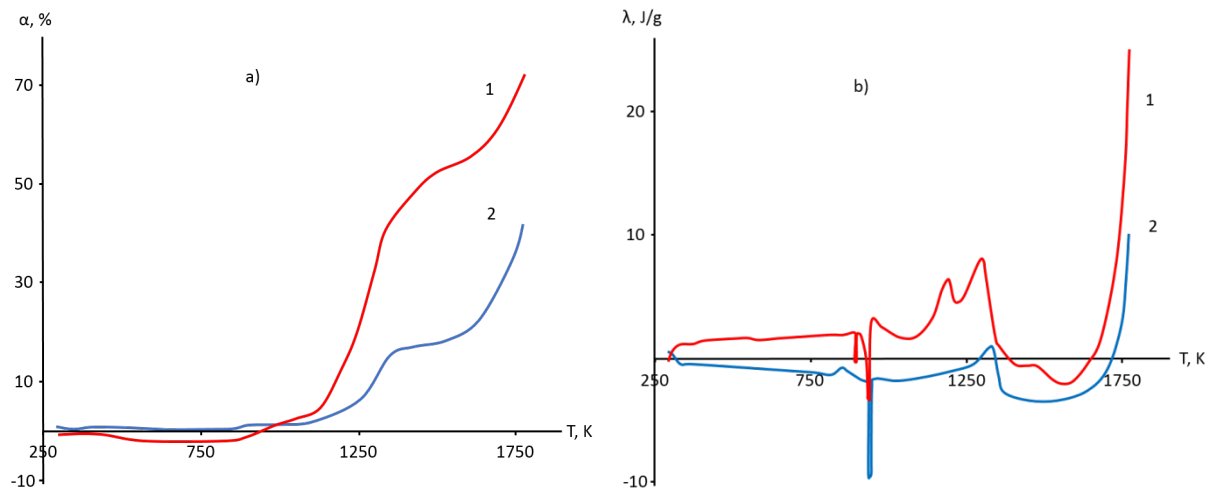


Figure 3. The TG (a) and DSC (b) curves: 1) - aluminum alloy with calcium; 2) pure aluminum; α - the completeness of oxidation.

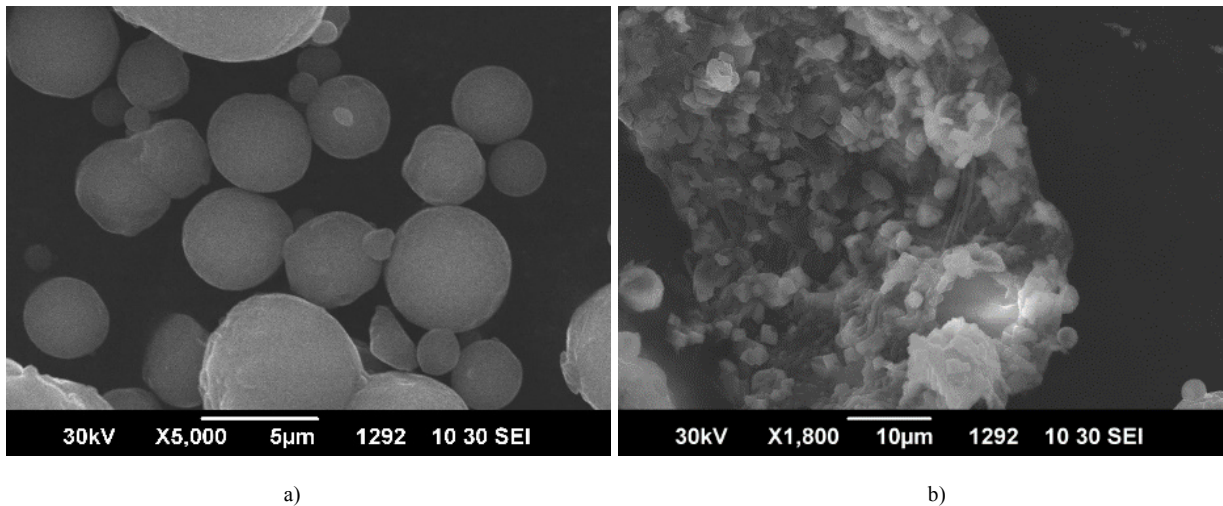


Figure 4. The morphology of aluminum alloy powder with calcium: a) initial; b) oxidized at 1273 K.

The data of electron microscopy showed that active interaction changed the morphology of spherical precursor particles. From spherical particles they transformed into agglomerates of smaller particles of oxidation products of different shapes (Fig. 4). For barium aluminum alloy powder [3], the particle morphology changed significantly (Fig. 5). However, in this case the changes were not so considerable since the degree of conversion at 1273 K is much lower than for Al-Ca powder, and the oxidation process did not reach the active site interaction (Fig. 6).

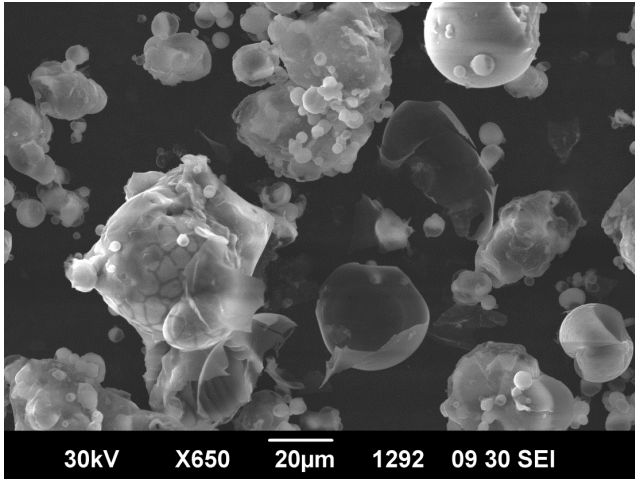


Figure 5. The particle morphology of Al-Ba powder oxidized during heating up to 1273 K.

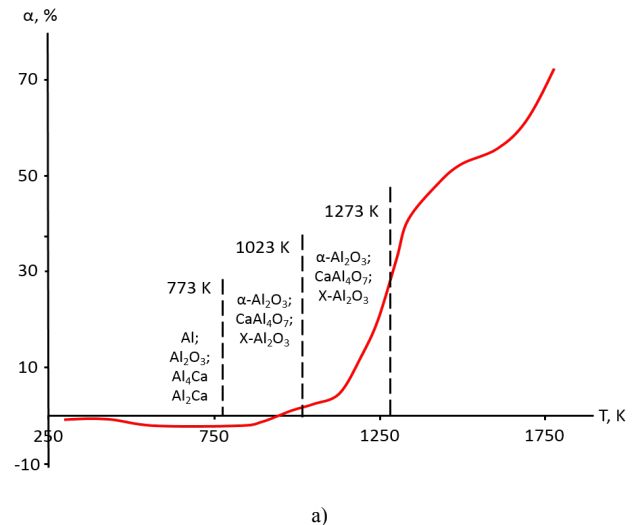
The obtained experimental results on Ca and Ba segregation on the surface of aluminum alloy powder particles, as well as the results of the study of phase formation during oxidation allow us to present a scheme of the interaction mechanism.

Figure 6 displays the curves of the transformation degree variation during oxidation of the powders and gives the regions of existence of phases present in the structure of the initial samples and formed during oxidation.

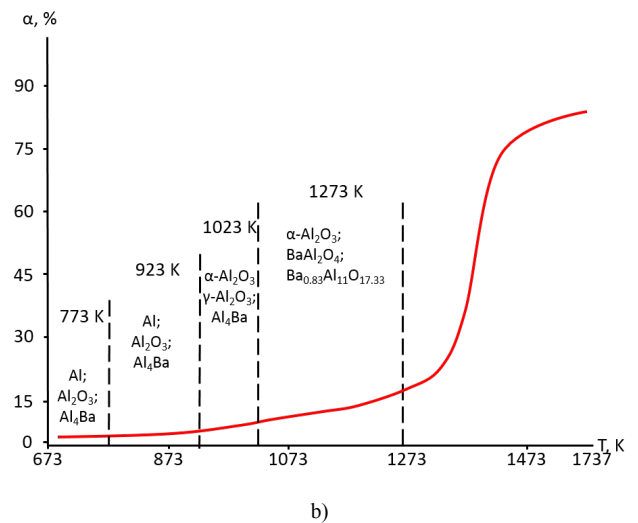
From Figure 6 it follows that the temperature intervals of active phase formation and the changes in the structure on the surface of particles and in the volume of the metal core correspond to the oxidation acceleration regions.

Table 1 shows some of the physical characteristics of the metallic and oxide phases in the structure and formed in the process of oxidation of the investigated aluminum alloy with calcium and barium.

where: d - the density of the metallic or oxide phase; z - the number of formula units; n - the number of metal atoms in the unit cell volume; V_u - the volume of a unit cell; V - the molar volume; γ - the molar ratio of volumes; Δ - the ratio of the comparison volumes of the obtained and the initial materials.



a)



b)

Figure 6. The TG curves of alloys: a) Al-Ca; b) Al-Ba; α – the completeness of oxidation

From Table 1 follows that the formed double oxides have crystalline structures differ from the structure of the intermetallic compounds on the surface of which they form, and the structure of the individual oxides of the alloy components.

Thus, the primary cause of oxidation acceleration in the examined powders is continuous changing of the phase composition accompanied by structural changes in the oxidation product layer on the surface of particles of aluminum alloy powders with calcium and barium. The mechanism of the influence of Ca and Ba on the process of oxidation of disperse aluminum is explained by their high surface activity with respect to aluminum, which increases their concentration on the reaction surface of the powder, as well as the completeness and speed of the interaction because the barrier layer on the particle surface loses its protective properties.

Table 1. The physical characteristics of the obtained phases

Metal, oxide	d, g/cm ³	z	n	V _u	V	γ	Δ	The cell
Al	2.697	4	4	66.4	10	-	-	Cubic; a=4.0494
γ-Al ₂ O ₃	3.61	10.7	21.4	493.04	28.24	3.71	1.41	Cubic; a=7.9
α-Al ₂ O ₃	3.98	6	12	279.6	25.62	0.28	0.91	Rhombohedral; a=4.76; c=12.99
Al ₂ Ca	2.405	8	24	519.33	39.1	-	-	Cubic; a=8.038
CaAl ₄ O ₇	2.88	4	20	546.27	90.28	0.21	1.38	Monoclinic; a=12.94; b=8.91; c=5.446
Al ₄ Ca	2.329	2	10	211.01	63.55	-	-	Tetragonal; a=4.362; c=11.09
CaAl ₄ O ₇	2.88	4	20	546.27	90.28	0.52	1.42	Monoclinic; a=12.94; b=8.91; c=5.446
Al ₄ Ba	3.49	2	10	234.48	70.27	-	-	Tetragonal; a=4.565; c=11.252
BaAl ₂ O ₄	4.094	2	6	208	62.36	0.3	1.48	Hexagonal; a=5.218; c=8.781
Al ₄ Ba	3.49	2	10	234.48	70.27	-	-	Tetragonal; a=4.565; c=11.252
Ba _{0.83} Al ₁₁ O _{17.33}	3.72	2	22.166	617.03	184.96	0.24	1.19	Hexagonal; a=5.587; c=22.721

In Fig. 7, four modifiers: V₂O₅ · nH₂O and NH₄VO₃ + HOCH₂CH₂OH studied by authors [10, 11], Ca and Ba are compared. It is seen that, depending on the type of modifier and the modification method, high completeness of oxidation were obtained. For example, for the more active powders the use of ethylene glycol is preferable.

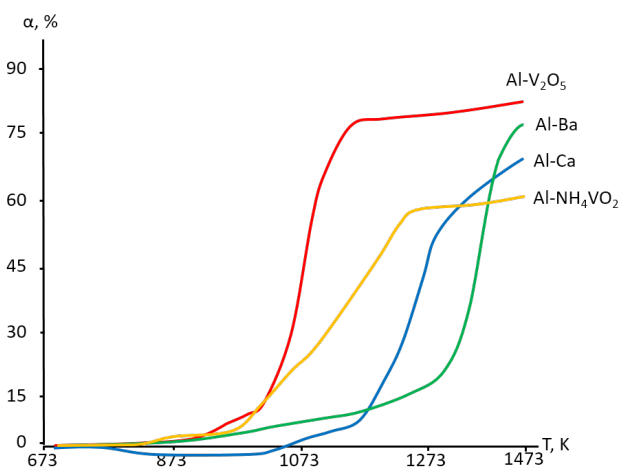


Figure 7. The TG curves of alloys: Al-V₂O₅, Al-Ba, Al-Ca, Al-NH₄VO₂; α – the completeness of oxidation.

3. Conclusions

1. Using synchrotron radiation diffraction, we were the first to study the sequence of changes in the phase composition of the oxidation products on the surface and in the volume of powder particles based on aluminum alloys containing 0.88 at.% Ca and 0.26 at.% Ba directly during oxidation in air at a heating rate of 10 K/min.

2. It was established that the high reactivity of the dopants, along with surface activity with respect to aluminum (surface segregation), promotes oxidation activation.

3. It is shown that, the active oxidation areas of the powders correspond to the structural and phase rearrangements in the metal core of the particles and in the oxidation products on their surface.

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