SCIENTIFIC BASIS OF INNOVATION

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PROCESSING OF ALUMINUM SLAG WITH THE USE OF SODA

Introduction. *It is known that light aluminum scrap and waste from aluminum production are difficult to melt effectively because aluminum is oxidized very easily.*

Problem Statement. *The technology for obtaining aluminum by reducing foundry slags allows a significant decrease in the amount of waste and a reduction in the cost of electricity for the production of castings.*

Purpose. *The purpose is to develop theoretical and technological framework for processing aluminum waste and obtaining high-quality product from it.*

Material and Methods. *300 g foundry slag is taken to determine the yield of aluminum from melting in an induction furnace. The reagent (caustic soda 2.0% by mass of slag) is calcined at a temperature of 250 °C for 1 hour to remove moisture and organic impurities. The slag is placed in an alund crucible and heated, with soda added at 700 °C. After that, liquid aluminum is poured into a mold and after crystallization it is weighed on analytical balances. Samples for chemical and spectral analyzes of aluminum are taken in accordance with GOST 7565-81. The structural transformations and phase transitions during heating and cooling of aluminum samples have been studied by differential scanning calorimetry (STA 449F1 Jupiter synchronous thermal analyzer by NETZSCH).*

Results. *At the level of a hypothesis, a mechanism of the metallurgical slag processing, which is based on the change in the valence of aluminum from (III) to (I) and vice versa, depending on the reaction temperature has been proposed. The regularities of the yield during the processing of low-grade aluminum-containing slags have been established. It has been shown that with the intensification of heat exchange processes, the range of optimal parameters decreases, while the yield increases. The phase transitions of aluminum samples obtained during the processing of foundry aluminum slag have been studied. It has been proven that this method of processing allows obtaining aluminum of a relatively high purity.*

Conclusions. *The results of the research can be used to improve the technology for obtaining secondary aluminum from aluminum production waste.*

Keywords: aluminum, foundry slag, yield, temperature, phase transitions.

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A significant increase in the use of aluminum products leads to the accumulation of waste that is used for the production of secondary aluminum alloys. As compared with primary metal, their production costs are much lower. The slags and chips, which are formed in the process of casting and processing of aluminum alloys, are processed at specialized enterprises. Foundry aluminum slag is formed in the surface layer and is a mix of foam that contains the products of the interaction of aluminum with air components. The slag is removed before entering the melt. According to various data, the content of pure metal (or alloy) in it is within 7—10% wt. metallic aluminum, 70—75% wt. aluminum oxide and various impurities. This type of slag is processed at non-ferrous metallurgy enterprises. The process mainly consists of the following stages: a) crushing of slag; b) fractional division of slag; c) water leaching of crushed slag; d) filtering of the solution in order to separate the salt solution and the solid residue; e) evaporation of a solid solution; g) drying; h) incineration of solid residue.

As mentioned above, light aluminum scrap is difficult to melt efficiently because it is oxidized very easily. In this regard, one of the most common technologies for processing aluminum waste is a process related to the protection of aluminum scrap from oxidation, for example, through immersing the crushed mix in molten aluminum. The methods and devices for implementing this technology of aluminum waste processing have been presented in [1—11].

To reduce the costs of processing aluminum slags, a method of pressing them in a hot state immediately after taking them from the mirror of the melting furnace has been proposed [12]. According to the developed technology, hot slag is loaded into a mold and pressed under a press. The extruded aluminum melt flows into a metal mold and solidifies. Smaller costs are required for processing the residue in the form of a pressed crust. However, the use of this technique only partially solves the problem of processing aluminum slag and reducing its share. The method does not allow separating aluminum during the processing of cold slags.

Aluminum slag is one of the main types of aluminum raw materials. Ferroaluminum and ferroaluminum silicon can be obtained from poor and waste aluminum slags. Slags with a low salt content are first enriched, and then a concentrate containing about 90% Al is obtained with subsequent remelting. Slags containing about 25% aluminum can be remelted without preliminary treatment.

Several salt-free slag purification processes have been known from the literature [14]. It has been shown that aluminum slag in the process of primary and secondary processing is formed due to the interaction of the molten metal with the furnace atmosphere [15]. The use of salt fluxes in modern production conditions entails a complex of similar problems, such as high cost and environmental hazards [16, 17]. Salt slags have been a significant environmental problem since 1995 [18], and in 2021, this problem has become even more acute. Other disadvantage is the fact that during melting the salts evaporate, which very often leads to overgrowth of the furnace lining. In addition, any salt requires energy for its melting and costs for purchase and transportation [19].

Furnaces of various designs are used for melting aluminum scrap, slag, and waste of various productions. Each of them is more or less suitable for melting a certain type of raw material. This is mainly due to the content of impurities, as well as to the reduction of burnout and the mechanization of the main technological operations.

Universal *reverberatory* furnaces are the most widely used. Almost any raw material can be melted in them. They can be of several modifications: one-, two- or three-chamber one. Two-chamber furnaces are most often used in industry.

For melting small charges, namely chips, slag, etc. rotating short-drum furnaces are interesting. It is a steel lined drum that is mounted on support rollers. The drum rotation speed is adjustable from one to eight rpm. The lining is stuffed or lined with a special shaped brick. The furnace is heated with the use of natural gas or fuel oil.

Aluminum slag is often processed in a DC electric slag furnace that has a crucible with the lower electrode as a cathode and the upper electrode as an anode [13]. Cryolite (Na_3AlF_6) and aluminum oxide are loaded into a crucible and melted, with subsequent addition of crushed aluminum slag (a mechanical mix of Al_2O_3 and metallic aluminum) to the resulting liquid melt (electrolyte) and cryolite, in portions, as they melt and dissolve in the electrolyte. The liquid metal is taken at the bottom of the crucible, in the cathode area, while the secondary slag in the form of a mix of cryolite and alumina is taken in the anode area. Therefore, the use of an electric slag furnace provides melting and dissolution of aluminum slag at a temperature in the range from 800 to 2000 °C. However, a significant disadvantage of this type of furnaces are their low remelting performance, increased costs and significant problems associated with air pollution by gases produced during the melting of cryolite.

It is known that reducing the amount of slag in the aluminum melting process is one of the main tasks of foundries. The maximum extraction of aluminum from it, which was previously removed from the melt, and which is outside the furnace, is another important task. Special drainage devices for separating aluminum from slag are effective only in combination with the cooling technology. The old method for cooling slag is to cool it on the workshop floor. The advanced methods include the use of inert gases and special presses.

The efficiency of slag cooling depends significantly on its activity. For example, slags containing magnesium are characterized by increased activity. Another factor is the amount and chemical composition of the fluxes in it. Without the use of cooling, its activity increases and the of slag burning process leads to rapid losses of the base metal. Very often it turns into oxides.

The technology for obtaining aluminum by reducing foundry slags allows a significant decrease in the amount of waste and a reduction in the cost of electricity for the production of castings.

Thus, the research is aimed at developing the theoretical and technological foundations of processing aluminum waste and obtaining high-quality products from it.

To determine the yield of aluminum, 300 g foundry slag is used per one melting. Melting is carried out in an induction furnace. Alundum is placed in a graphite crucible, the bottom between graphite and alundum is lined with aluminum oxide powder. After that, the graphite crucible is insulated from the outside with kaolin wool and inserted inside a copper induction coil that is cooled by water. The high-frequency generator VChG-15 serves as source of high-frequency electric current supplied to the induction coil. The temperature in the crucible before the beginning of chemical reactions is measured by a tungsten-rhenium thermocouple BP 5/20. Caustic soda, sodium chloride, and lime in amount of 2.0—2.2% of the slag mass are used as reagents. Slag, Na_2CO_3, NaCl, and $CaCO_3$ are calcined in a SNOL

Table 1. **The Quantitative Analysis of Raw Materials**

No.	Al, % wt.	Al_2O_3, % wt.	SiO_2, % wt.	Fe_2O_3, % wt.	CuO, % wt.	MgO, % wt.	MnO, % wt.	Σ adm., % wt.
1	36.68	57.34	1.81	2.47	0.23	0.07	0.08	1.32
2	32.48	58.12	5.71	1.82	0.27	0.07	0.09	1.44
3	36.86	57.57	1.82	1.80	0.26	0.05	0.07	1.57
4	35.20	59.11	1.56	2.45	0.11	0.05	0.08	1.43
5	36.58	58.14	1.63	1.81	0.25	0.04	0.05	1.50
6	34.25	59.01	1.79	2.51	0.86	0.04	0.07	1.47
7	33.98	57.18	2.44	4.74	0.30	0.07	0.06	1.23

Fig. 1. General appearance of raw materials (*a*), samples of aluminum (*b*) and slag obtained after melting (*c*)

1.6.2.0.0.8/9 M1 muffle furnace at a temperature of 250 °C for one hour to remove moisture and organic impurities. The slag dried in this way is placed in an alund crucible and heated. When a temperature of 700 °C is reached, the reagents that bind aluminum and silicon oxides into aluminates and silicates are added to the slag. After that, liquid aluminum is poured into a mold and, after cooling, weighed with analytical scales.

The samples for chemical and spectral analyzes of aluminum are made according to GOST 7565-81 [20]. The quantitative analysis of raw materials is given in Table 1.

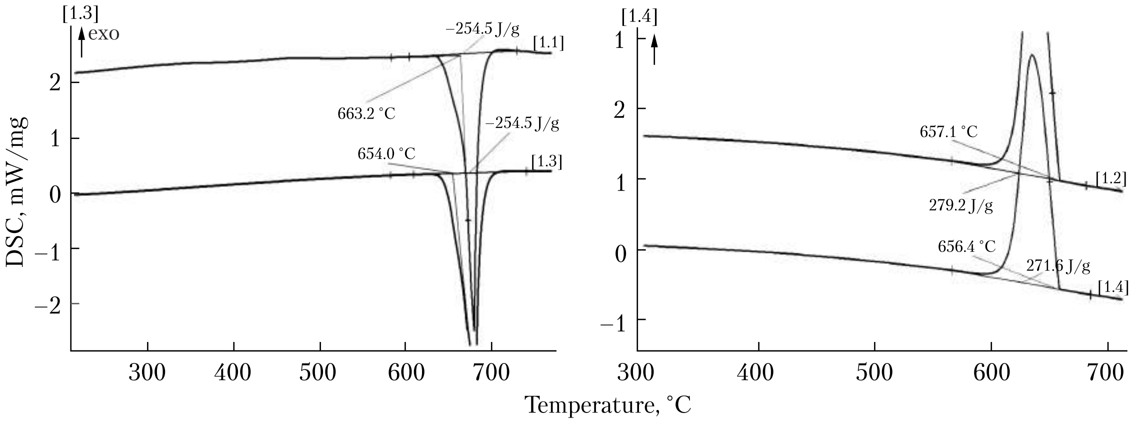
Differential scanning calorimetry (DSC) is used to study structural transformations and phase transition during heating and cooling. The experiments are carried out with the use of a synchronous thermal analyzer STA 449F1 Jupiter of NETZSCH (Germany) [21]. The thermal analyzer allows conducting research in the two modes: "sample" (without taking into account the thermophysical properties of the crucible system) and "sample with correction" (given the thermophysical properties of the crucible). In the "sample" mode, the studies are carried out in comparison with an inert reference that has the thermophysical properties similar to those of the studied sample.

To carry out research in the "sample with correction" mode, changes in the heat capacity of the crucible system and in the reference are investigated in the same conditions (atmosphere, heating rate, temperature interval) under which the sample is planned to be studied, and then the device do measurements given these parameters.

Table 2. **The Chemical Composition of the Obtained Samples and Their Yield**

Sample No.	Si, % wt.	Fe, % wt.	Cu, % wt.	Mg, % wt.	Mn, % wt.	Aluminum extraction coefficient, %
1	0.28	0.34	0.053	0.022	0.017	40
1*	0.22	0.26	0.060	0.016	0.014	52
2	0.89	0.25	0.063	0.014	0.020	55
3	0.28	0.35	0.048	0.016	0.015	61
4	0.18	0.31	0.028	0.016	0.011	42
5	0.23	0.25	0.060	0.012	0.031	49
6	0.27	0.32	0.230	0.013	0.018	47
7	0.38	0.65	0.079	0.019	0.025	50

Note: 1* is the sample obtained as a result of melting in a graphite crucible.



a *b*

Fig. 2. DSC-curves of aluminum sample No. 1 during heating (*a*) and cooling (*b*)

In this way, it is possible to eliminate the influence of the crucible and partly of the reference on the research results. It is almost impossible to choose an ideal reference, even if a heat-treated sample (in which there are no structural changes any longer) made of the same material as the studied sample is used as reference. Because of the different weight, shape, and location in the crucible, the influence of the reference is noticeable, which leads to the slope of the baseline and some distortion of the DSC curves.

The yield of aluminum is determined with 2.0% wt. caustic soda (Na_2CO_3) [22, 23]. The general appearance of the raw material, aluminum samples, and the slag obtained after melting is given in Fig. 1. The chemical analysis of the slag has shown that it mainly consists of sodium aluminate.

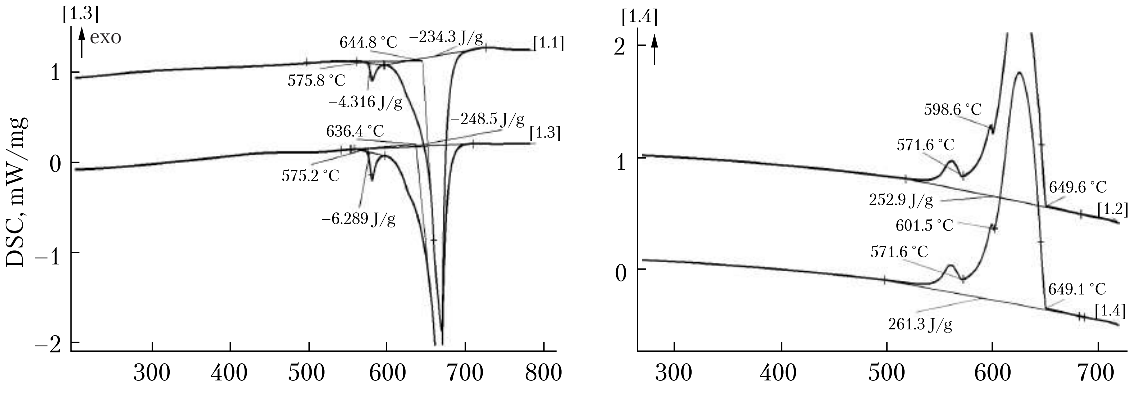
The aluminum samples obtained in this way have been analyzed by the two methods: the X-ray spectral technique and the electron scanning spectroscopy. The chemical composition of samples and the yield of aluminum are given in Table 2.

Table 3. **The Parameters of the Phase Transitions of Aluminum Samples**

Sample no.	T_m (1), °C	T_m (2), °C	T_{cr} (1), °C	T_{cr} (2), °C	H_m (1), J/g	H_m (2), J/g	H_{cr} (1), J/g	H_{cr} (2), J/g
1	663.2	654.0	651.1	656.4	−254.5	−263.6	279.2	271.6
2	644.8	636.4	649.6	649.1	−234.3	−248.5	252.9	261.3
3	659.8	652.9	656.5	656.0	−237.6	−247.6	258.0	256.2
4	669.5	654.6	657.4	657.1	−249.9	−245.1	240.3	239.4
5	651.4	649.7	653.7	653.3	−184.4	−179.1	185.8	186.6
6	655.8	648.4	654.5	654.5	−223.1	−220.7	229.4	223.9
7	658.0	643.6	653.8	653.2	−234.1	−241.6	248.2	248.6
8^*	660.6	660.1	656.8	656.7	−244.3	−237.6	242.4	245.8

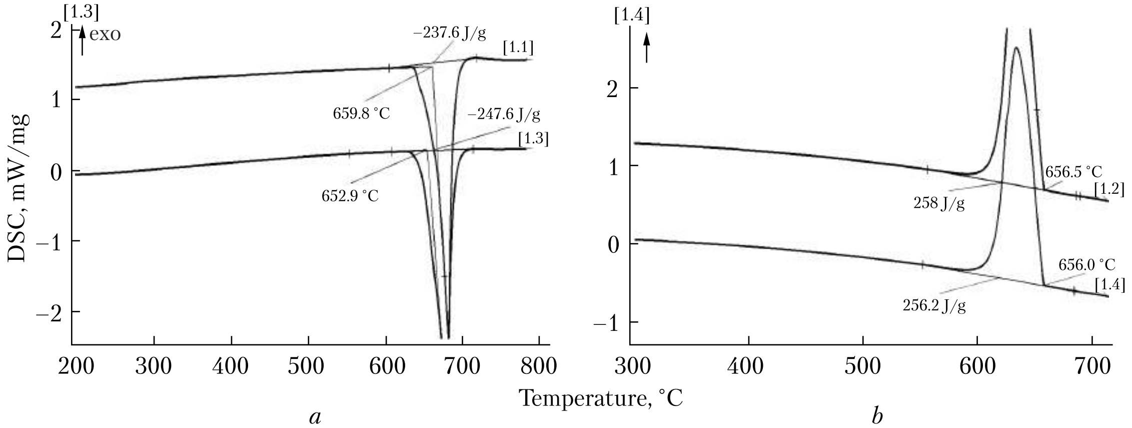
Note. T_m (1), T_m (2) are the temperatures of the first and the second melting process; T_{cr} (1), T_{cr} (2) are the crystallization temperatures after the first and the second melting; H_m (1), H_m (2) are the enthalpies of the first and the second melting processes; H_{cr} (1), H_{cr} (2) are the enthalpies of crystallization after the first and the second melting.

1. Sample 8* is standard aluminum grade A85. Its chemical composition is as follows: Al ≥ 99.8; Fe ≤ 0.08; Si ≤ 0.06; Ga ≤ 0.03; Mg ≤ 0.02; Mn ≤ 0.02; Zn ≤ 0.02; Cu ≤ 0.01; Ti ≤ 0.008. 2. The chemical composition of samples 1—7 is given in Table 2.



a *b*

Fig. 3. DSC-curves of aluminum sample No. 2 during heating (*a*) and cooling (*b*)



a *b*

Fig. 4. DSC-curves of aluminum sample No. 3 during heating (*a*) and cooling (*b*)

The mechanism of this process is based on a change in the valence of aluminum from three to one and vice versa, depending on the reaction temperature. It can be represented by the following chemical reactions:

$$2Al_2O_3 + Na_2CO_3 = 2NaAlO_2 + Al_2O +$$
$$+ CO_2 + O_2 \ (t = 2500\text{–}3000\ ^\circ C)$$

After the process described above, the temperature is lowered to 1000–1100 °C. At the same time, monovalent aluminum oxide decomposes into metallic aluminum and trivalent aluminum oxide:

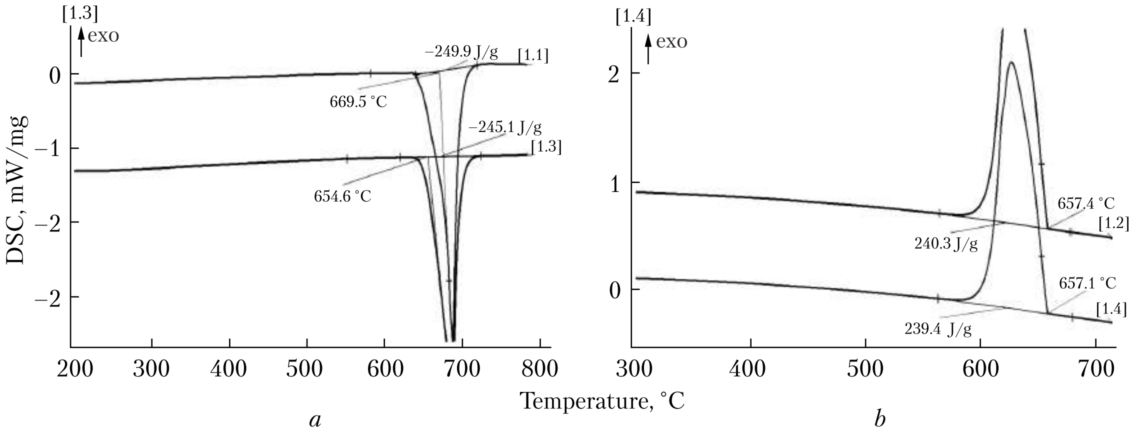
$$3Al_2O = 4Al + Al_2O_3$$

Regarding the joint action of chloride and sodium carbonate, first NaCl interacts with aluminum oxide with the formation of sodium oxide and aluminum chloride, then Na_2O converts Al_2O_3 into aluminate:

$$Al_2O_3 + 6NaCl = 3Na_2O + 2AlCl_3$$
$$Na_2O + Al_2O_3 = 2NaAlO_2$$

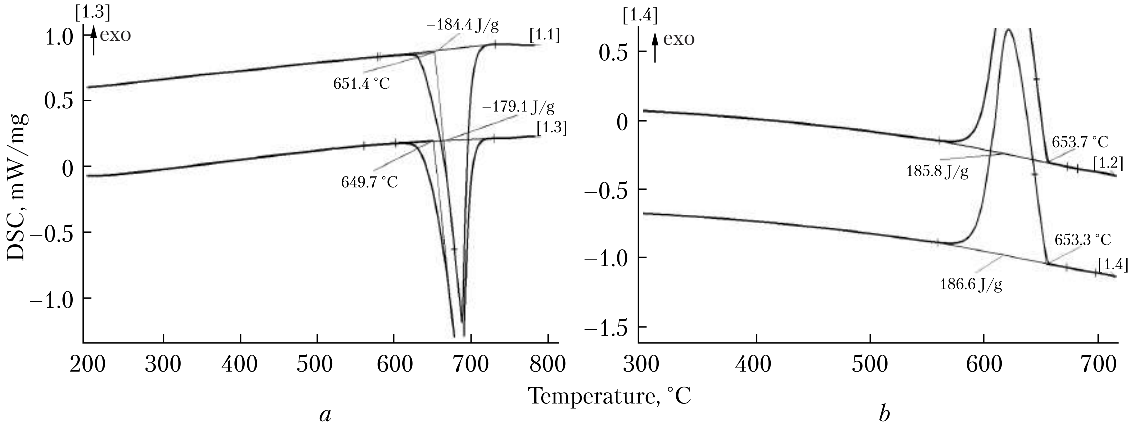
Along with this, the phase transitions of the above-mentioned aluminum samples have been studied.

The obtained results are presented in Table 3 and Figs 2–9. It can be seen that the temperature and enthalpy of the phase transitions do not significantly differ from those of standard aluminum (A85). They indicate that the processing of aluminum foundry slag using the above method leads to obtaining aluminum of a relatively high



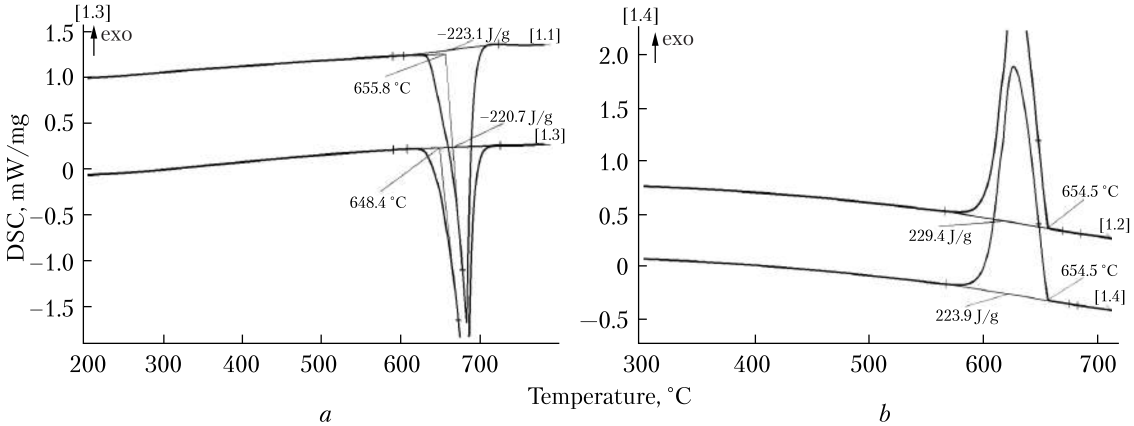
a *b*

Fig. 5. DSC-curves of aluminum sample No. 4 during heating (*a*) and cooling (*b*)



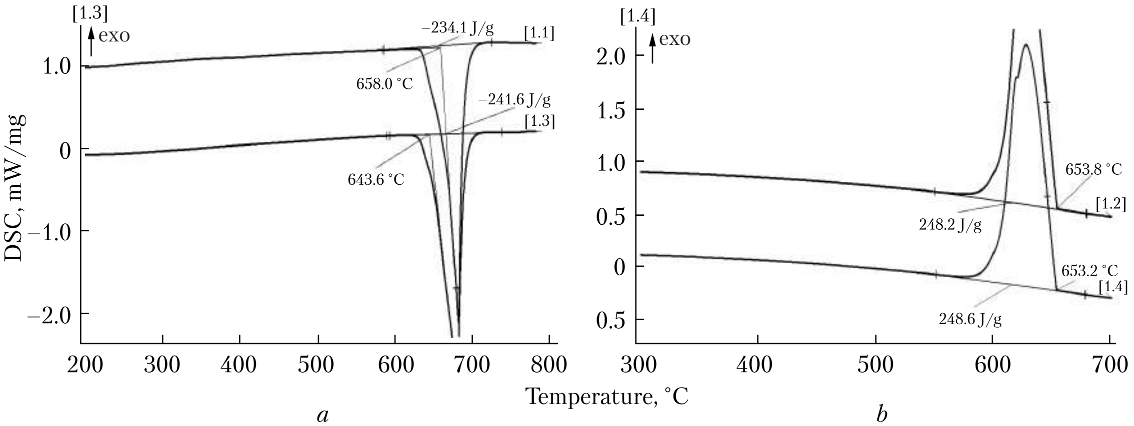
a *b*

Fig. 6. DSC-curves of aluminum sample No. 5 during heating (*a*) and cooling (*b*)



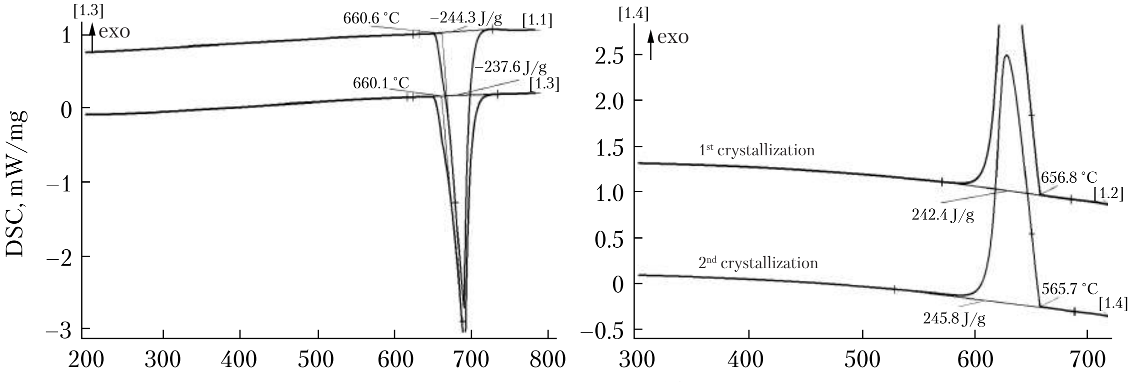
a *b*

Fig. 7. DSC-curves of aluminum sample No. 6 during heating (*a*) and cooling (*b*)



a *b*

Fig. 8. DSC-curves of aluminum sample No. 7 during heating (*a*) and cooling (*b*)



a *b*

Fig. 9. DSC-curves of aluminum sample No. 8 during heating (*a*) and cooling (*b*)

purity. The exceptions are the enthalpies of sample 5. They differ by approximately 60 J/g. This is probably because of the presence of impurities in this material.

As for aluminum sample number 2, there are several peaks on the differential melting and crystallization curves. The peak at a temperature of 574 ± 2 °C is associated with the formation of Al-Si eutectic that, according to calculations, is about 7.8%. From the diagram of the states of aluminum-silicon, it can be seen that at a content of 12.2% Si, the melt turns into a liquid state at a temperature of 577 °C [24, 25]. In addition to aluminum, other chemical elements are present in this system (see Table 2).

The effect of sodium carbonate on the yield of aluminum from foundry slag has studied. In this case, the yield of aluminum is approximately 49—51%. The phase transitions of aluminum samples obtained as a result of processing foundry aluminum slag have been studied by the differential scanning calorimetry. It has been confirmed that the use of this method enables obtaining aluminum of a relatively high purity.

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ОСОБЛИВОСТІ ПЕРЕРОБКИ АЛЮМІНІЄВОГО ШЛАКУ СОДОВИМ МЕТОДОМ

Вступ. Відомо, що легкий алюмінієвий брухт і відходи алюмінієвого виробництва важко ефективно плавити, оскільки він дуже легко окислюється.

Проблематика. Технологія одержання алюмінію шляхом відновлення ливарних шлаків дозволяє суттєво зменшити кількість відходів, знизити витрати електроенергії на виробництво виливок.

Мета. Розробка теоретичних і технологічних основ переробки алюмінієвих відходів та одержання з них високоякісного продукту.

Матеріали й методи. Для визначення металургійного виходу алюмінію однієї плавки в індукційній печі брали 300 г ливарного шлаку. Реагент (каустичну соду 2,0 % від маси шлаку) прожарювали при температурі 250 °С протягом 1 год для видалення вологи та органічних домішок. Шлак поміщали в алундовий тигель та включали нагрів, а при 700 °С додавали соду. Після цього рідкий алюміній заливали у форму й після кристалізації його зважували на аналітичних терезах. Проби для хімічного та спектрального аналізів алюмінію брали згідно з ГОСТ 7565-81. Дослідження структурних і фазових перетворень при нагріванні й охолодженні алюмінієвих зразків проводили диференціально скануючою калориметрією (синхронний термічний аналізатор *STA* 449F1 *Jupiter* фірми *NETZSCH*).

Результати. На рівні гіпотези розроблено механізм процесу переробки металургійного шлаку, який базується на зміні валентності алюмінію з (III) до (I) і навпаки, залежно від температури протікання реакцій. Встановлено закономірності величини металургійного виходу при переробці низькосортних алюмінійвмісних шлаків. Показано, що при інтенсифікації процесів теплообміну діапазон оптимальних значень параметрів зменшується, а величина металургійного виходу зростає. Досліджено фазові переходи алюмінієвих зразків, які одержано при переробці ливарного алюмінієвого шлаку. Доведено, що такий метод переробки дозволяє отримати алюміній порівняно високої чистоти.

Висновки. Результати роботи можна використовувати для удосконалення технології одержання вторинного алюмінію з відходів алюмінієвого виробництва.

Ключові слова: алюміній, ливарний шлак, металургійний вихід, температура, фазові переходи.