# DEVELOPMENT AND INVESTIGATION OF THE TECHNOLOGICAL PROCESS OF PLASMA CARBOTHERMAL REDUCTION OF SLAG FROM SECONDARY METALLURGY OF ALUMINUM

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## Abstract

Based on a critical analysis of the current state and prospects of development of the problem of pyrometallurgical recovery/extraction of aluminum from aluminum-bearing industrial waste, the need to replace traditional, electrocarbonothermic processes and melting process units with innovative, plasma carbothermal processes and furnace-reactors, with the possibility of reverse feeding and recovery of gasified during melting metal and metal oxide components is substantiated. On the basis of this analysis a new technological scheme of smelting with a new design of plasma-arc furnace-reactor, which provides a solution to the problem using a special hollow double-shell graphite cathode connected to the system of circulating supply of gases separated from the reaction zone, was developed and presented. The proposed technological scheme also differs in the use of such highly active liquid and gaseous reagents as carbon-containing reducing agents as calcium carbide ($CaC_2$) and methane ($CH_4$). The main features of chemism of reducing processes are described. It is shown that by replacing traditional coke with anodized calcium carbide and natural gas (methane) the recovery rate of aluminum oxide (Al 29-34%) and silica ($SiO_2$) and hematite ($Fe_2O_3$) present with it increases to 80-99%. Specific power consumption is reduced by 35-40%, the 90-95% reduction in the loss of target elements, the 80% reduction in the emission of greenhouse carbon dioxide, which is replaced by a very valuable recyclable synthesis gas - $CO-H_2$. By additionally feeding separate portions of quartzite and steel-rolling scale in the furnace-reactor, a complex alloy-ligature of Fe-Si-Al-Ca system is melted, with the ratio of components: 1:[1.3-2]:[1.3-1.2]:[0.9-1.25]. With the introduction into industrial practice of the plasma carbothermal process of aluminum reduction from secondary aluminum dumping slags

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accumulated in the world (4 million tons/year), it will be possible to return up to 1-1.5 million tons/year of aluminum to the production processing cycle.

**Keywords:** secondary aluminum slag; recycling; aluminum recovery; plasmacarbothermia; complex ferroalloys.

## Introduction

According to the International Aluminum Institute (IAI), despite the socioeconomic crisis caused by the COVID 19 pandemic, global aluminum production in 2020-21 increased by 2.6-3% compared to the same period in 2019 and 1.8-2% compared to 2018. According to the same organization, total global primary aluminum production has increased by more than 50% in the last decade, owing primarily to China, India, and the Gulf countries. As a result of this growth, the aluminum industry now ranks first among non-ferrous metallurgy segments and second overall in metallurgy. According to the most recent statistics, global aluminum consumption ranks second only to steel production in terms of volume, totaling up to 65 million tons per year.

According to IAI forecasts, as the global economy grows, urbanization, increased consumption of goods, and infrastructure construction increase, demand for aluminum will increase by more than 40% in the coming decades (until 2050). As a result, the increase in aluminum-bearing waste generated by this industry is unavoidable. According to projections [1, 2], secondary aluminum production will account for more than 60% of total aluminum production by 2050-60. As a result, the aluminum industry will be forced to focus on the development and implementation of specialized production facilities adapted for the processing of secondary raw materials and technogeneous waste in the near future.

## The merits and advantages of aluminum and aluminum-based alloys

Aluminum and alloys based on it have the following advantages: low density, high strength, thermal and electrical conductivity, corrosion resistance, manufacturability, and light weight. Aluminum alloys' high level of structural and operational properties allow them to be widely implemented in a variety of industries, including mechanical engineering, electrical engineering, shipbuilding, aerospace engineering, food industry, construction, and so on [3].

Aluminum alloys are increasingly being used in the production of packaging, particularly beverage cans. The majority of products made from aluminum and its alloys are used in mechanical engineering (35-45%). The urban construction industry ranks second in terms of aluminum consumption (30%). Aluminum is used extensively in the production of various types of packaging (20-25%) [4].

Automotive casting is growing the fastest. A modern car's cast parts made of various alloys account for up to 50-60% of its mass (the number of such parts would reach up to 300 items). The car's total cost includes up to 20% of the cost of cast parts. Aluminum alloy parts can weigh up to 150-250 kg in modern passenger car models [5].

As an example, the casting of an engine block made of cast iron weighs up to 75 kg on average, while that of an aluminum alloy weighs only 25 kg. After machining, a cast iron part can weigh up to 45 kg, while an aluminum part can weigh as little as 15 kg. As a result, a massive weight reduction (by a factor of three) can be achieved on just this one production position. This is significant because every 10% reduction in vehicle

weight results in a 5% reduction in gasoline consumption. Experts believe that using light alloy parts in conjunction with carbon fiber products instead of cast iron and steel will reduce vehicle weight by 60% on average. This is critical because it will be possible to save 2-2.5 liters of gasoline per 100 kilometers [6].

Similar trends can be seen in the railway transportation and construction industries. For example, the development of "aluminum" light passenger carriages increases train movement on the railway line by up to two times [7,8]. Furthermore, it is well known that the use of aluminum structures in construction contributes to a significant reduction in the load on the foundation when high-rise buildings and other large-scale structures are built. According to various sources, the service life of aluminum load-bearing structures is up to 250-300 years, and buildings constructed with them can withstand earthquakes of up to 9 points [9].

Semi-finished products derived from aluminum wrought alloys are also widely used in the construction of formwork in monolithic houses. Moreover, structural elements of the "aluminum" formwork would be reused and easily recycled. To improve thermal insulation efficiency, load-bearing frames made of aluminum profiles are used, between which modern lightweight heat-insulating materials are sandwiched, followed by decorative facing made of clad aluminum sheets or composite panels based on them [10].

## Recyclability of aluminum. tasking the study

Aluminum can compete with steels, cast irons, copper alloys, plastics, and concrete because it can be recycled numerous times. Aluminum obtained from ore would be remelted many times and used to manufacture new products using appropriate technologies. According to various data, secondary aluminum requires 2.5-6 times less raw materials than primary metal. To produce one ton of aluminum from ore, 13,000-15,000 kW/h of power is required, whereas scrap and waste remelting requires only 200-550 kW/h. Simultaneously, the cost of aluminum alloys would be reduced by 30-50% [11, 12].

According to current estimates, approximately 20 million tons of secondary aluminum are produced worldwide each year. The United States, Japan, Germany, France, and Italy are the world leaders in the use of recycled aluminum. Simultaneously, 4 million tons of aluminum-bearing oxide slags are formed per year. The total aluminum content of these slags ranges from 10% to 80%. After mechanical extraction of metallic aluminum inclusions from these slags (10-11%), a significant portion of them is buried in special landfills [13]. In addition to occupying a relatively large area during burial, slag has a negative impact on the ecosystem as a source of toxic substance emission [14].

Based on the above-mentioned analytical review, it can be confidently stated that the observed trend of a steady increase in the consumption of products made from aluminum and aluminum alloys in almost all industries will result in a steady increase in the amount of generated aluminum-bearing slags, exacerbating the need to develop environmentally friendly and economically viable recycling technologies. This emphasizes the problem's urgency and gives it a special urgency.

The author's studies [15, 16] present a generalized theoretical model and methodological foundations for diagnosing the effectiveness and optimizing the organizational and economic system for recycling of metal-containing waste. The algorithm developed is universal and applicable to all types of technologically generated metal-bearing waste, including aluminum.

Currently, in order to solve the problem of aluminum recovery and recycling, the task of identifying the most promising, cost-effective, and environmentally friendly advanced technology for its recovery, with a concurrent analysis of the technical possibilities for its further improvement, thereby extending the life cycle of aluminum and, as a result, - increasing the specific share of secondary aluminum circulating in the global economy, is underway.

In terms of managing the technical, economic, and environmental efficiency of recycling, the most important (productive) mechanism of influence is the degree of target metal extraction, the specific energy consumption per ton of the resulting product, and the level of secondary harmful impact on the ecosystem. The primary goal of this research is to lay the scientific and technical groundwork for the intensification of the target aluminum reduction process, ensuring maximum extraction/extension of the life cycle while minimizing energy consumption and negative environmental impacts.

## Advanced, environmentally friendly recovery technologies

An examination of the current state of aluminum-bearing slag processing reveals that, in terms of highly efficient environmentally friendly recycling of aluminum-bearing industrial waste, technologies for direct (salt-free) carbothermal reduction of aluminum deserve special consideration. According to studies [17-19], the use of salt fluxes in the production of secondary aluminum is unacceptable not only from an ecological standpoint, but also from a resource conservation standpoint, because: a) approximately $100 is required for the disposal of 1 ton of salt slag; b) approximately 50% of the metal caught in salt slags is irretrievably lost; and d) all aluminum oxide is irretrievably lost. A technology for the electrothermal processing of aluminum slags is proposed in the study [20], which involves the use of forcedly circulating molten aluminum accumulated in a special storage bath as the extracting phase. The study [21] proposes alternative approaches.

According to the findings of this study, advanced, environmentally friendly technologies for the processing of aluminum slags should include the establishment of conditions that ensure the coagulation of oxide particles, which would be implemented in the following options: a) Blowing the melt with water vapor, or b) exposing the melt to additives containing calcium oxide. The use of such technology in the practice of secondary aluminum raw materials processing will allow not only for effective metal extraction, but also for the production of loose (self-dispersing) secondary slags, from which residual metal inclusions are mechanically extracted using a simple classification operation on vibrating screens. Metal fractions larger than 1.5-1.6 mm would be directly returned to the metallurgical processing or foundry production process in this case, as they easily merge during melting.

According to studies [22-24], the recycling of aluminum-bearing secondary oxide materials and the secondary application of extracted aluminum would achieve particularly high and stable efficiency in the carbothermal production of special deoxidizing agents, ligatures, and modifiers of cast iron and steel, particularly in the smelting of non-standard complex multicomponent ferroalloys of the Fe-Si-Mn-Al system. On the one hand, the aforementioned approach extends the life cycle of this essential valuable metal, and on the other, by deoxidizing and improving the quality of the treated steel, it serves as an auxiliary tool for extending the service life of products and structures made from it. Studies [25, 26] emphasize the importance of extending the life cycle of aluminum by

improving the technological processes of its production and primary and secondary applications.

It is noteworthy that direct carbothermal reduction of aluminum by solid carbon of coke is highly effective under conditions of limited access of atmospheric oxygen to smelting products, in traditional as well as in modified (shaft) ore-thermal furnaces, and in DC plasma-arc furnaces [27, 28]. According to the study [29], the reduction of aluminum at normal atmospheric pressure is also possible by using such a non-solid (gas) reagent as methane.

The use of methane in carbothermal metal reduction processes is of great scientific and practical interest because it reduces the release of reactive greenhouse carbon dioxide, replacing it with a very valuable high-energy synthesis gas with a molar ratio of $H_2$:CO = 2 and water vapor. This gas can then be reused as a power gas for combustion and heating/drying-sintering of sinter charge, as a material for boiler houses and steam generators, as a secondary gas-phase reducing agent for iron reduction in shaft furnaces, and so on. The benefit of the aforementioned approach is undeniable, as it would lead to an increase in energy efficiency and a decrease in carbon dioxide emissions, which has received special attention from the global community in recent decades [30, 31].

To emphasize the metallurgical value of the aforementioned aluminum-bearing slags and the feasibility of methane reduction, it is necessary to mention the possibility and efficiency of direct carbothermal reduction of silicon and iron from the corresponding oxide compounds or waste [32, 33]. It is important to emphasize this because silicon and iron oxides are almost always present with the target aluminum oxide in the metallurgical slags of the aluminum industry and, according to the studies [22, 23, 24, 34], this would be considered a very positive, auxiliary factor for their joint recovery, increasing the degree of extraction of valuable aluminum and receiving special multicomponent ligatures with high added value that are in demand by the industry.

A review of the references mentioned above, on the one hand, and the results of our own theoretical and experimental work on the carbothermal reduction of metal oxides [23, 35, 36, 37], on the other, show that for small-scale production of target alloys, it is more convenient to conduct reduction reactions in a specially modernized plasma-chemical arc furnace-reactor, with the possibility of simultaneous supply of solid and gas-phase carbonaceous reducing agents.

## Rational technical solution to improve the recovery process

A systematic examination of the options for accelerating the recovery process while minimizing the environmental impact revealed that the primary goal is to maximize the efficiency of the application of methane and the synthesis gas released when reacting with metal oxides that have a high potential for recovery under appropriate thermodynamic conditions. In this regard, the mentioned plasma-arc melting technology of special plasma-chemical arc furnace-reactors with one liquid-metal bottom electrode provides the possibility of reverse vertical supply of the mentioned gas reagents [37]. In addition, we added a special side tuyere directed to the high-temperature reaction zone, with the possibility of injection and diffusion of methane in the melt's oxide layer, for the implementation of gas-phase reduction processes in the reactor-furnace (active power 100 kVA). Purging also contributes to the intensification of the process of mixing of the interacting melt components and eliminates the need for high-energy side electromagnetic mixers (solenoids). The angle of methane purge from the side tuyere can vary between

25 and 35 degrees depending on the chemical composition and viscosity of the melted alloy.

The modernized furnace-reactor, schematically is illustrated in Fig. 1, consists of the following main structural and functional-technological elements: 1 – cathode unit; 2 – starting double-walled tubular anode; 3 – reaction chamber-crucible; 4 – high-temperature arc – plasma discharge; 4' - an annular channel for reverse blowing of gasified melting components; 5 – channels for supplying primary orifice gas ($CO_2$), 6 – pockets for supplying processing raw materials; 7 – channel for the output of a mixture of reaction gases/gas-phase components (GPC – gas-phase components); 8 – liquid-phase slag-metal mixture; 9 – liquid metal anode; 10 – slag notch; 11 – metal notch; 12 – tuyere for injection of methane.
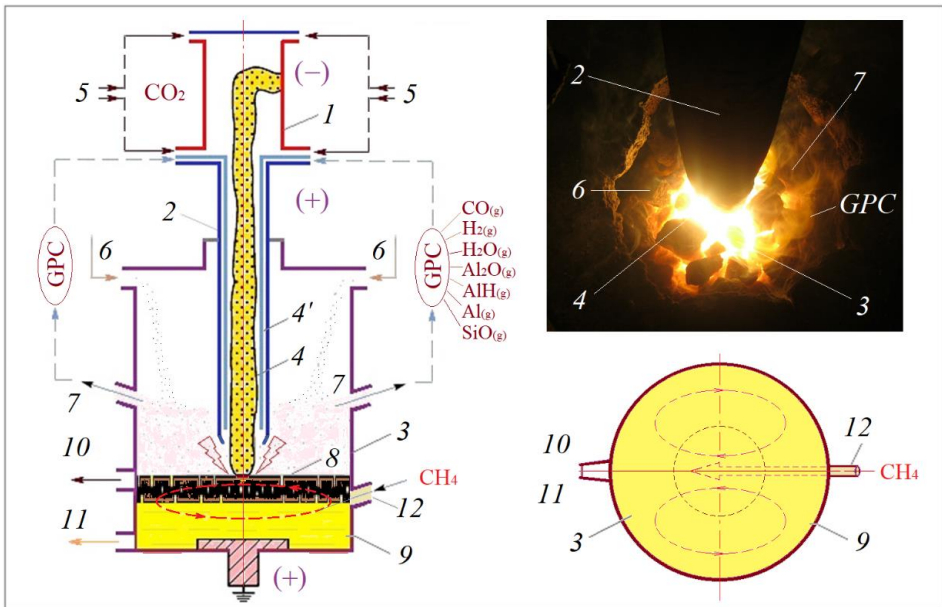


*Fig. 1. Plasma-chemical reactor-furnace with one liquid-metal bottom electrode: schematic diagram of functioning and the process of melting at the initial stage of the restoration of metals from the processed metallurgical slag (designation see in the text above).*

Unlike the well-known melting technology, which uses a previously prepared melt from the target (extractable) metal (in this case, - aluminum) as a liquid-metal seed electrode, we use a previously melted active reducing agent such as calcium carbide ($Ca_2C$, carbon content 35-37%, smelting temperature 1900-2100 °C, power consumption 3000 kWh/t). This allows us to perform carbothermic reduction processes with carbon dissolved in calcium carbide, which sharply reduces idle waste and volatilization, increasing the degree of useful application. Simultaneously, calcium carbide is introduced into the resulting complex alloy, which contributes to an increase in the activity and value of the smelted complex deoxidizer, desulfurizer, and degasser. The use of solid-phase calcium carbide as an active reducing agent in ferrous and non-ferrous metal metallurgy has already been reported in studies [38, 39], but in the process we are developing and

studying, it is used in a liquid state as a boiling (wetting), heat accumulating, and activated carbon-reduction layer.
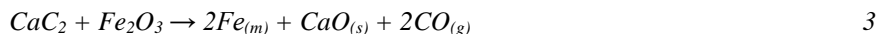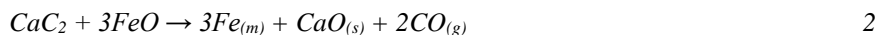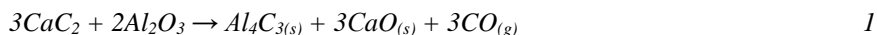
The recovered metal melt 9, as a heavier fraction of the melt, accumulates in the lower part of the crucible and is drained into the receiver via the tap-hole 11. The metal is not completely drained, leaving a "swamp" that protects the furnace's ceramic hearth and the end electrode inserted in it from the action of the reactive oxide melt 8. Tap hole 10 is used to remove larger amounts of slag that have accumulated.

In turn, the study [40] substantiates the efficiency of using the target for us complex multi-component ligature, the joint content of aluminum, silicon, and calcium, where it is shown that the deoxidation of liquid steel with a silico-aluminum-calcium complex alloy leads to the formation of more fusible non-metallic compounds of the system $CaO$-$SiO_2$-$Al_2O_3$, with a melting point of 1300±50 °C that have the property

## Features of chemism of the developed plasma carbothermal process

Features of chemism, providing the intensification of the process of reduction of metal oxides from aluminum-bearing slag, would be represented by the following stoichiometric equations:

At the first stage of melting, in the temperature range 1900 < T < 2000 (°C), when the main components of the charge are supplied in liquid-phase calcium carbide, occur the following reactions [38, 41]:

$$3CaC_2 + 2Al_2O_3 \rightarrow Al_4C_{3(s)} + 3CaO_{(s)} + 3CO_{(g)} \qquad\qquad 1$$

$$CaC_2 + 3FeO \rightarrow 3Fe_{(m)} + CaO_{(s)} + 2CO_{(g)} \qquad\qquad 2$$

$$CaC_2 + Fe_2O_3 \rightarrow 2Fe_{(m)} + CaO_{(s)} + 2CO_{(g)} \qquad\qquad 3$$

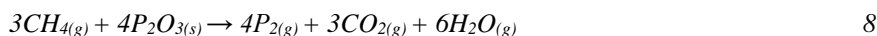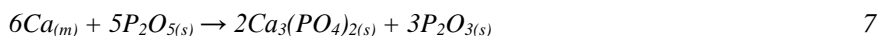$$CaC_2 + SiO_2 \rightarrow Si_{(m)} + Ca_{(m)} + 2CO_{(g)} \qquad\qquad 4$$

When calcium carbide reacted with the target oxides and the consumption of carbon in a volume of the stoichiometric required amount, the chemical equilibrium of the initial reactions were violated [42]:

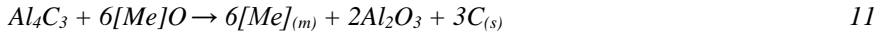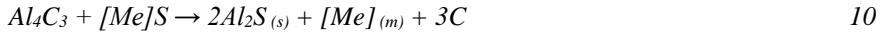$$CaO_{(s)} + 3C \rightarrow CaC_{2(m)} + CO_{(g)} \qquad\qquad 5$$

subsequently, the formed lack of carbon, calcium oxide is replenishing from the methane supplied in the melt [43]:

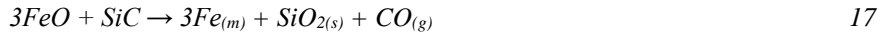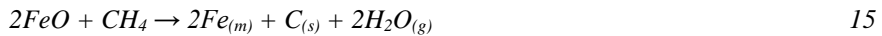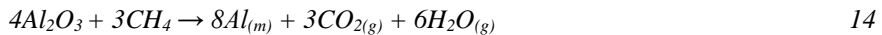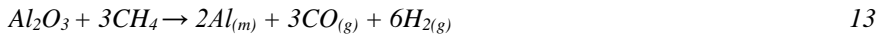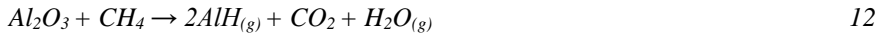$$CaO_{(s)} + 2CH_4 \rightarrow CaC_{2(m)} + H_2O_{(g)} + 3H_{2(g)} \qquad\qquad 6$$
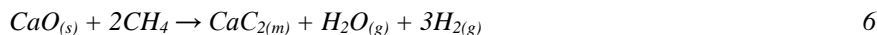
Elemental (metallic) calcium isolated in the melt according to reaction (4) with supplied methane leads to intense dephosphorization of the melted alloy [43, 44]:
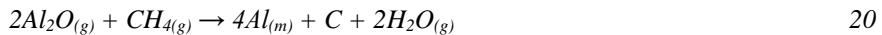
$$6Ca_{(m)} + 5P_2O_{5(s)} \rightarrow 2Ca_3(PO_4)_{2(s)} + 3P_2O_{3(s)} \qquad\qquad 7$$

$$3CH_{4(g)} + 4P_2O_{3(s)} \rightarrow 4P_{2(g)} + 3CO_{2(g)} + 6H_2O_{(g)} \qquad\qquad 8$$

In turn, the aluminum carbide compound $Al_4C_3$ formed by reaction (1) at a temperature T > 2000 °C determines the desulfurization of the metal melt [Me](m) as well as the reduction of the remaining amount of their oxides [45]:

$$Al_4C_3 + 6S \rightarrow 2Al_2S_{3(s)} + 3C \qquad\qquad\qquad\qquad 9$$

$$Al_4C_3 + [Me]S \rightarrow 2Al_2S_{(s)} + [Me]_{(m)} + 3C \qquad\qquad\qquad 10$$

$$Al_4C_3 + 6[Me]O \rightarrow 6[Me]_{(m)} + 2Al_2O_3 + 3C_{(s)} \qquad\qquad 11$$

In parallel, while stirring the melt (slag-metal mixture) with methane blown into it, occur auxiliary reduction reactions (second stage):

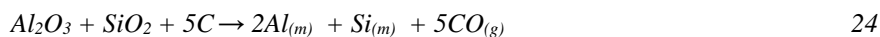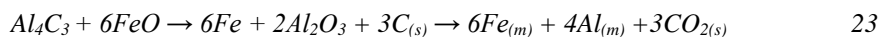$$Al_2O_3 + CH_4 \rightarrow 2AlH_{(g)} + CO_2 + H_2O_{(g)} \qquad\qquad\qquad 12$$

$$Al_2O_3 + 3CH_4 \rightarrow 2Al_{(m)} + 3CO_{(g)} + 6H_{2(g)} \qquad\qquad\qquad 13$$

$$4Al_2O_3 + 3CH_4 \rightarrow 8Al_{(m)} + 3CO_{2(g)} + 6H_2O_{(g)} \qquad\qquad 14$$

$$2FeO + CH_4 \rightarrow 2Fe_{(m)} + C_{(s)} + 2H_2O_{(g)} \qquad\qquad\qquad 15$$

$$SiO_2 + CH_4 \rightarrow SiC_{(s)} + 2H_2O_{(g)} \qquad\qquad\qquad\qquad 16$$

$$3FeO + SiC \rightarrow 3Fe_{(m)} + SiO_{2(s)} + CO_{(g)} \qquad\qquad\qquad 17$$

In turn, the gas-phase components (AlH, $Al_2O$, Al) formed in the zone of plasma-arc exposure (T ≥ 2500 °C) at their reverse vertical blowing/supply in the crucible of the reactor-furnace, in the presence of methane supplied from the bottom, initiate the following reactions [46]:

$$Al_2O_{3(s)} + 2AlH_{(g)} \rightarrow 2Al_2O_{(g)} + H_2O_{(g)} \qquad\qquad\qquad 18$$

$$Al_2O_{(g)} + 2AlH_{(g)} \rightarrow 4Al_{(m)} + H_2O_{(g)} \qquad\qquad\qquad\qquad 19$$

$$2Al_2O_{(g)} + CH_{4(g)} \rightarrow 4Al_{(m)} + C + 2H_2O_{(g)} \qquad\qquad\qquad 20$$

$$2Al_2O_{(g)} + 5C \rightarrow Al_4C_{3(s)} + 2CO_{(g)} \qquad\qquad\qquad\qquad 21$$

At the same time, secondary aluminum carbide formed by reaction (21), after condensation and dissolution in slag, began to react with both primary and secondary oxides of the present metals (11), restoring their additional portions:

$$Al_4C_3 + Al_2O_3 \rightarrow 6Al_{(m)} + 3CO_{(g)} \qquad\qquad\qquad\qquad 22$$

$$Al_4C_3 + 6FeO \rightarrow 6Fe + 2Al_2O_3 + 3C_{(s)} \rightarrow 6Fe_{(m)} + 4Al_{(m)} + 3CO_{2(s)} \qquad 23$$

$$Al_2O_3 + SiO_2 + 5C \rightarrow 2Al_{(m)} + Si_{(m)} + 5CO_{(g)} \qquad 24$$

At the same time, the $CO-H_2$ syngas released as a result of reduction reactions served as a protective-reducing atmosphere and prevented the formation and penetration of elemental (gas) oxygen from outside. In parallel, the mentioned syngas reacted with such gasified components as $SiO$ and $Al_2O$, reducing them to metal phases.

$$SiO + CO \rightarrow Si + CO_2 \qquad 25$$

$$SiO + H_2 \rightarrow Si + H_2O \qquad 26$$

$$Al_2O + H_2 \rightarrow 2Al + H_2O \qquad 27$$

From an energy and environmental point of view, it should be mentioned that excess portions of syngas would be used to produce a very valuable energy product, methanol [47]. This feature of the technology being developed would be considered as its additional significant advantage over traditional carbothermal metal reduction processes, since, according to preliminary calculations, it leads to a reduction in reactive greenhouse gas ($CO_2$) emissions by about 90%.

## Experimental studies, results and discussion

As object of experimental research was selected aluminum-bearing slag accumulated as a result of remelting aluminum scrap from aluminum structures and items, accumulated in the ash dumps of the former Rustavi plant "Tsentrolit" and "Gegmeti" Ltd. The general chemical analysis of these slags after their mechanical separation and extraction of metal inclusions (Fig. 2) showed in Table 1.

*Table 1. Chemical composition of slag.*

| Aluminum slag | Content of Elements, % | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Al | Fe | Si | Ca | Cr | Mn | Pb | Sb | Zn | S | P |
| | 31.5 | 13.5 | 4.5 | 0.79 | 0.73 | 0.145 | 0.063 | 0.043 | 0.034 | 0.093 | 0.015 |

The technological modes were controlled during experimental melting in a laboratory plasma-arc furnace-reactor (Fig. 1) using standard control and diagnostic equipment (Ammeters, Voltmeters, Wattmeters, Pressure gauges, Linear stroke meter, Transformer stage switches, Adjustable current limiters, Electromagnetic starters, and so on). The metal, slag, and dust-like formations formed during melting were examined using optical and electron scanning microscopy, as well as X-ray phase and spectral analysis.

*Fig. 2. Aluminum-bearing slag before sorting and mechanical separation (extraction) of metal inclusions, with a particle size of 1-50 mm (1) and after, - particles with a size of 0-5 mm (2).*

Aluminum slag - 100-75 kg, Calcium carbide - 40-45 kg, Quartzite - 55-75 kg, and Steel mill scale - 10 kg were the solid-phase components of the charge used for experimental melts. As a result, the specific proportion of Calcium carbide required for the initial stage of melting was 20-25% of the total mass of the processed solid charge. The remaining solid components of the charge are: a) crushed Aluminum slag obtained after mechanical separation, containing 56-65% $Al_2O_3$, 10-11% $SiO_2$, 19-20% $Fe_2O_3$; b) crushed (-1 mm) quartzite ($SiO_2$ 96%) in the amount of 20-25%; and d) degreased Steel mill scale in the amount of 5% (Fe - 70-75%).

Table 2 presents refined quantitative data on the consumption of the experimental charge's main components, the chemical composition of the smelted complex alloy, and the main technological parameters of its melting, with an average content of the target aluminum oxide in the processed slag of 60% (Al - 31.7%). Figure 3 depicts the fracture morphology, macro and microstructure of the ingot obtained as a result of ingot casting.

*Table 2\*. The variation in melted composition and degree of extraction in correlation with different components of charge.*

| Smelting No. | Main components of charge and their proportion, kg | | | | Consumption of methane on kg oxide raw materials, l | Power consumption, kW.h/kg | Composition of main elements in the melted allow, weight % | | | | Degree of extraction /reduction of target metals, % | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Aluminum slag | Calcium carbide | Steel mill scale | Quartzite | | | Al | Ca | Fe | Si | Al | Ca | Fe | Si |
| 1 | 100 | 40 | 10 | 54 | 37.5 | 6285 | 28.03 | 20.73 | 21.52 | 28.05 | 88.32 | 82.90 | 99.64 | 99.25 |
| 2 | 95 | 41 | 10 | 58.5 | 38 | 6250 | 26.67 | 21.13 | 20.82 | 29.85 | 88.45 | 82.45 | 99.70 | 99.42 |
| 3 | 90 | 42 | 10 | 62 | 38.5 | 6225 | 25.28 | 21.59 | 20.11 | 31.21 | 88.51 | 82.23 | 99.74 | 99.54 |
| 4 | 85 | 43 | 10 | 66 | 39 | 6195 | 24.21 | 21.96 | 19.40 | 32.78 | 89.75 | 81.70 | 99.78 | 99.63 |
| 5 | 80 | 44 | 10 | 70 | 39.5 | 6170 | 22.91 | 22.34 | 18.69 | 34.34 | 90.23 | 81.25 | 99.83 | 99.70 |
| 6 | 75 | 45 | 10 | 75 | 40 | 6150 | 21.65 | 22.64 | 17.97 | 36.34 | 90.95 | 80.51 | 99.85 | 99.75 |

\* Separate data on the content of carbon, sulfur, and phosphorus in the resulting alloy are not stated due to their insignificant scatter C $\leq 1\%$, S $\leq 0.15\%$, P $\leq 0.01\%$.

The data in Table 2 demonstrate the high efficiency of the tested plasma-arc processing and complex, liquid and gas-phase metal oxide reduction technology. Aluminum extraction can reach 88-90%, silicon and iron extraction can reach 99%, and calcium extraction can reach 80-82%.

According to the data in Table 2, reducing the amount of aluminum slag supplied to the charge by 25% and increasing the specific proportion of calcium carbide and quartzite from 40 to 45 and 54 to 75 kg, respectively, reduces power consumption by 2.2% from 6285 to 6150 kWh/kg, while increasing methane consumption by 6.6% has a positive effect on extraction of aluminum, silicon, and iron. Among them, it is worth noting that the extraction of the target aluminum increases by 3%. The obtained complex alloy is distinguished by a high silicon and calcium content. Silicon content increased by 29.5%, from 28.05 to 36.34 wt%, and calcium content increased by 9%, from 20.73 to 22.64 wt%. This increases the metallurgical value of the alloy. The above characteristics demonstrate the plasma carbothermic reduction and metal recovery process's high technological flexibility, giving it a clear advantage over traditional smelting processes.

The obtained complex alloys can be conditionally marked as follows: melting No. 1 - $FeSi_{1.3}Al_{1.3}Ca_{0.9}$; No. 2 - $FeSi_{1.4}Al_{1.28}Ca$; No. 3 - $FeSi_{1.5}Al_{1.25}Ca$; No. 4 - $FeSi_{1.6}Al_{1.24}Ca_{1.1}$; No. 5 - $FeSi_{1.8}Al_{1.22}Ca_{1.19}$; No. 6 - $FeSi_2Al_{1.2}Ca_{1.25}$.

The DRON-4 X-ray diffractometer was used to analyze phase formation in these multi-component alloys, and the results show that the phase composition of the studied samples consists primarily of three phases: $AlFe_3Ca_2Si$ - a solid solution of aluminum, silicon, and calcium in iron (light gray eutectic matrix), $Al_2SiCa_{1.5}$ - a solid solution of silicon and calcium in aluminum (large bright white grains), and $FeSiCa_{0.5}$ (4).

A scanning electron microscopy (SEM) study in reverse scattered electron (BSE) recording mode confirms the presence of the marked phase components. Figure 4 depicts the relevant illustrations. In these SEM-BSE images with EDS-analysis data of the chemical composition of the formed phases (Tab. 3), it can be seen that the ingot is primarily composed of intermetallic phases: $AlFe_3Ca_2Si$ (Spectrum 5), $FeSiCa_{0.5}$ (Spectrum 2, 4), $Al_2SiCa_{1.5}$ (Spectrum 1, 3), but there, spectrum 6 detects imperceptible on the microstructure (Fig. 3(3)) finely grained intermetallic phase - $FeAl_{1.5}Si_{1.5}$, which occupies 1-1.5% of the studied surface.
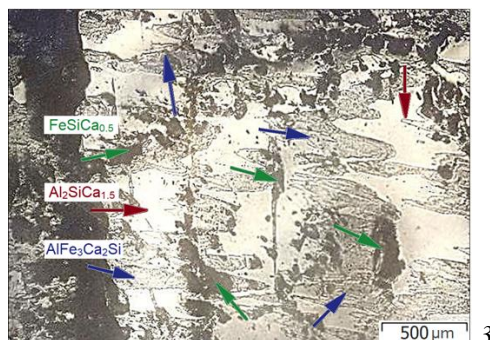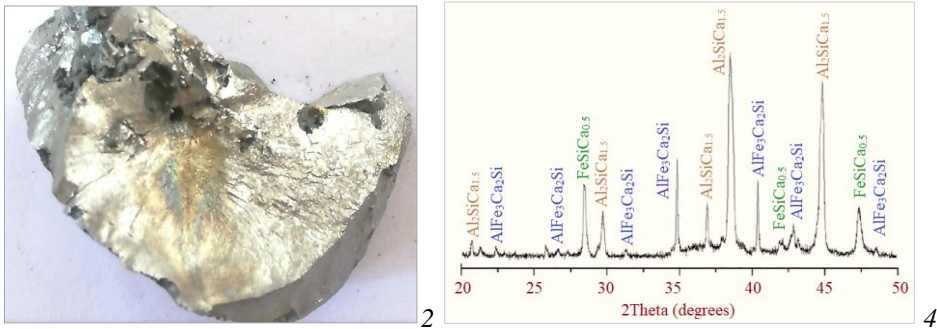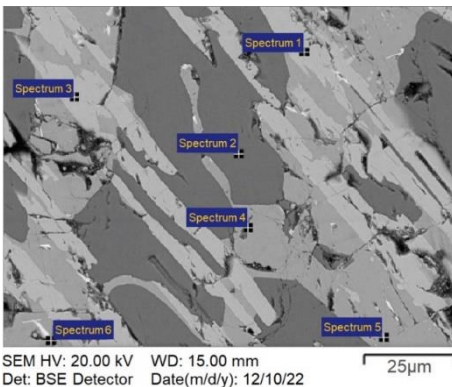
*Fig. 3. Fracture, macro-microstructure and X-ray diffractogram of an ingot from alloy No.1 - FeSi$_{1.3}$Al$_{1.3}$Ca$_{0.9}$ (Tab. 2).*

General view of the ingot during cooling (950 °C), x0.1; 2. Fracture of macrostructure after cooling, x0.45; 3. Microstructure, x250; 4. X-ray diffraction pattern.

*Table 3. Results of the EDS analysis*



| EDS Analysis | Result Type – Weight % | | | |
|---|---|---|---|---|
| Spectrum Label | Al | Si | Ca | Fe |
| Spectrum 1 | 42.61 | 21.42 | 31.53 | - |
| Spectrum 2 | - | 39.43 | 19.65 | 39.38 |
| Spectrum 3 | 43.25 | 22.13 | 32.12 | - |
| Spectrum 4 | - | 38.71 | 19.40 | 40.63 |
| Spectrum 5 | 14.19 | 14.84 | 27.84 | 41.12 |
| Spectrum 6 | 37.15 | 36.84 | - | 24.95 |

*Fig. 4. SEM-BSE micrograph and Tab. 3. EDS analysis of alloy No.1 (FeSi$_{1.3}$Al$_{1.3}$Ca$_{0.9}$).*

Figure 5 depicts data on the dependence of the gasified phases of the reacting components on the temperature of the exhaust gases. Based on this quantitative dependence, it is clear that their reverse supply is critical for optimizing the efficiency and productivity of the plasma-carbothermal reduction process. Figure 5 shows that when the temperature rises above 2450 ºC, the most intense gasification occurs.
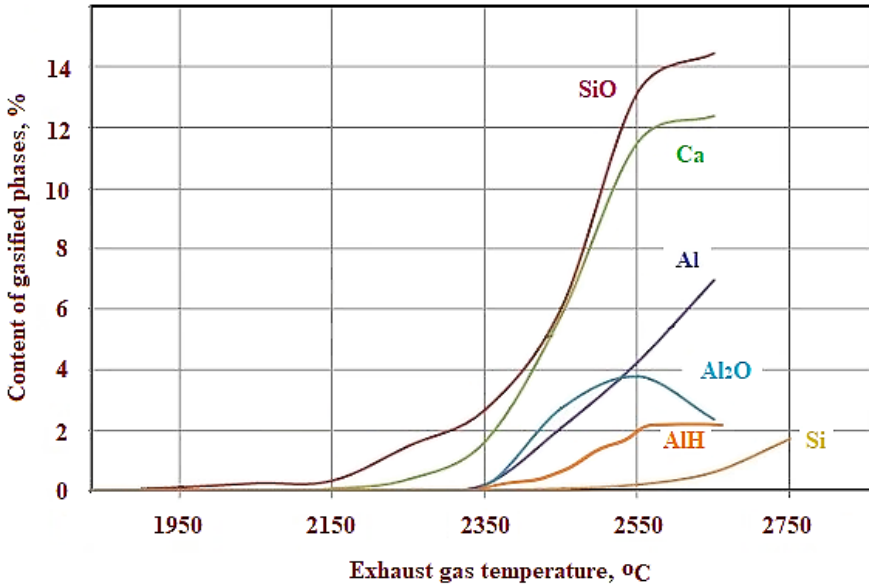
*Fig. 5. Influence of melting temperature on the intensity of gasification of the main components of the charge.*

During the experiments, it was discovered that the ratio of total carbon used for reduction and oxides of the reduced metals is also significant. The optimal ratio was found to be $O_{[Me]}:C \rightarrow 2.6 \pm 0.1$. The consumption of methane entering the melt was especially significant. An increase in methane consumption increased the amount of carbon supplied to the reaction zone, but due to the excessive formation of water vapor and slag coagulation, the depth and area of penetration of the plasma impact decreased, resulting in the inhibition of the melting process, a decrease in melt temperature, and a reduction in the degree of reduction (Fig. 6). Only calcium showed a positive effect as the intensity of secondary calcium carbide formation increased (Eq. 6). Melting takes 45-60 minutes on average, depending primarily on the power of the plasm arc (1500-1000 A, 36-45 V). The greatest depth and area of effective penetration of plasma effect on the treated charge was provided by the ratio of the electric voltage between the cathode and anode with the strength of the developed current source, equal to the value - 0.0324, according to the criteria of gasification intensity and recoverability of target elements. As shown in Fig. 7, the dependence of the degree of recovery of the target metals on the grain size of the starting secondary material also demonstrates the importance of the factor of the depth of exposure to plasma arc discharge. As shown in Fig. 7, increasing the grain size of the separated slag reduces metal recovery performance, which is undesirable. Laboratory smelting results show that the fraction less than 5 mm is most effective for plasma-arc processing.
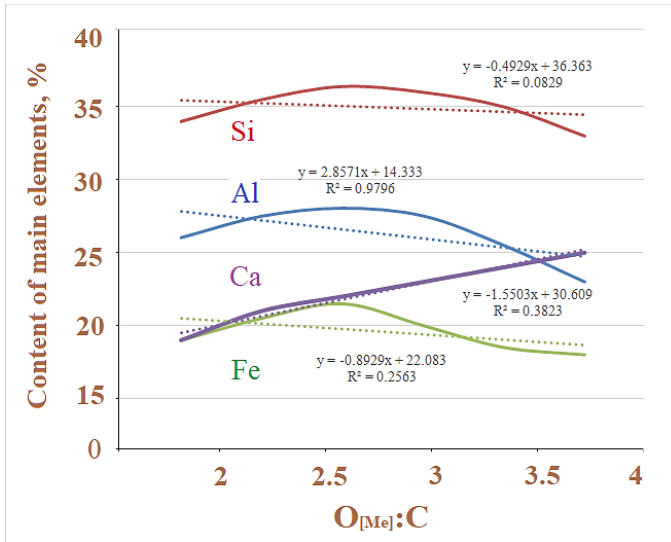
*Fig. 6. The influence of the ratio of the amount of oxygen introduced by the charge to the carbon of the used reducing agents on the content of the target metals in the resulting complex alloy.*
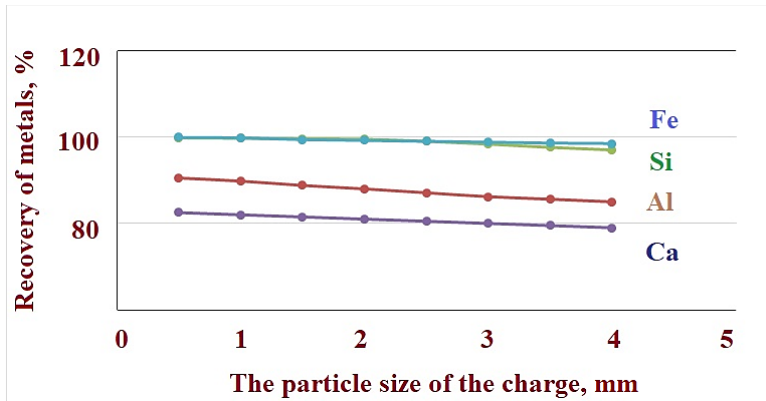


*Fig. 7. Influence of fractionation of aluminum slag on the degree of extraction of aluminum and related metals.*

Based on the above-mentioned research data, the developed and studied process of plasma-carbothermal reduction of aluminum slags would be considered the most promising, practical, feasible rational solution of the problem.

A comparative analysis of the technological parameters of the proposed plasma-carbothermal technological process with the traditional electrocabrothermal process for the reduction of aluminum-bearing slags clearly indicates on a significant advantage of the first. In particular, it becomes possible to effectively, environmentally friendly processing of fine-fraction aluminum-bearing oxide waste, without their pre-treatment and briquetting that improves the degree of recovery of the target aluminum and its

accompanying metals up to 10-15%, reduces the specific consumption of electrical energy by 35-40%, the waste and escape of target elements are reduced up to 90-95%, the emission of greenhouse carbon dioxide is reduced up to 80% and excreted very valuable synthesis gas – $CO·H_2$.

According to preliminary calculations, the prime cost of the plasma-cabothermal process for the reduction of aluminum-bearing metallurgical slags will be in the range of 800-1000 US dollars, which is approximately the same as the prime cost of standard large-tonnage ferroalloys. In contrast to market prices for the latter, the price of complex multicomponent alloys is several times higher, highlighting the viability of their industrial production.

It is worth noting that, taking into account the amount of aluminum-bearing oxide slags (4 million tons/year) formed in the world each year as mentioned in Chapter 3 and the possibility of their highly efficient reduction as stated in this study, global losses of aluminum from slag could be reduced by up to 0.8-0.4 million tons/year (by 80-90%). At the same time, newly formed (so-called recurrent) slags (20-10 wt.%) will not pose a significant environmental risk due to their high lime content and ability to self-disperse, as they will be suitable for use as hydro-active binder additives in the production of building cement and its derivatives.

## Conclusions

Proposed method of plasma-arc processing and complex, liquid and gas-phase extraction of Aluminum from Aluminum-bearing slag wastes can achieve degree of its extraction up to 88-90%, while extracting silicon and iron present in charge by 99% and calcium by 80-82%.

To achieve such a result, it is necessary:

- ratio of the amount of solid oxygen introduced into the plasma arc furnace-reactor with the total amount of carbon added by calcium carbide and methane is maintained at the level of 2.59-2.61;

- do not lower the temperature of the reaction zone below 2550 °C;

- to ensure this condition, the ratio of the voltage supplied at the cathode with the developed current must be kept at the level of – 0.0324.

## Declarations
**Conflict of Interest:** On behalf of all authors, the corresponding author states that there is no conflict of interest.

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