Remelting of highly polluted metallic aluminium scrap with ecological refining reagents

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Abstract. Questions about the impact of the metallurgical industry on the environment are increasingly raised in the modern developing world. There are production of harmful gaseous and solid emissions during refining, associated with the use of chloride, fluoride reagents during recycling of aluminium alloys from secondary raw materials on industry enterprises. The using of chlorides, fluorides compounds should be replaced by more environmentally friendly refining reagents or new approaches to production technologies that enable aluminium recycling facilities to meet real-time economic and environmental requirements. The article deals with the problems of the use of existing chloride and fluoride refining compositions, as well as studies and evaluation of highly contaminated remelting aluminium scrap using promising reagents that increase the environmental friendliness of the process. The information and research, incorporated in this article can be extrapolated on the remelting technology of secondary metallized aluminium raw materials in industrial metallurgical units.

Flux treatment is performed to remove alkali, alkaline earth metals, impurities, non-metallic inclusions, dissolved hydrogen, since they affect the final properties of the final product - an aluminium alloy. Salt fluxes NaCl – KCl, KCl with additions of fluorides and chlorides are commonly used [1, 2, 3]. Salt fluxes should have a low melting point, since they wet aluminium oxides at lower temperatures, increase the viscosity of slags and, thus, ensure their removal by creating a chemical reaction or by physicochemical separation [4]. The chemical composition and amount of salt are decisive factors determining the yield of the fitting product, efficiency and environmental friendliness of the process. The composition of the liquid flux must be monitored. The flux should not form a crust on the melt mirror when the impurities are wetted; therefore, some amounts of fluoride are usually introduced into the flux. For high silicon alloys, sodium fluoride is used. For alloys with a high magnesium content, magnesium chloride is used. On the reaction with magnesium oxide in the metal magnesium chloride forms magnesium oxychloride, which remains in the slag. But since magnesium chloride tends to absorb moisture, it is used along with salts. This reduces the risk of moisture absorption. The authors found that a mixture of 1/3 of sodium chloride, potassium chloride, and magnesium chloride is the most effective. If magnesium is present in the alloy as an impurity, it can be extracted by degassing using chlorine gas, hydrochloric acid gas, silicon fluoride gas, boron gas fluoride. The temperature required for the implementation of these processes above 800°C [5]. The authors of [6] investigated the effect on cleaning, microstructure, and properties of the A00 melt with C2Cl6 and a number of other fluxes. In the melt analyzed together with C2Cl6, several cracks and significant porosity were detected in the surface
oxide film, which led to an increase in melting losses. In addition, the slag mainly consisted of pure aluminium and aluminium oxide. The size of the inclusion was not less than 10 microns and from 100 to 150 microns in the grain size, stretched in the body of the casting. These smaller inclusions did not adversely affect the strength, but had an adverse effect on the relative elongation. Zhao et al. [7] studied the behavior of gas bubbles in aluminium alloys in the process of remelting by observation using microfocus radiography. Experimental observation shows that double remelting has a positive effect on degassing. In addition to this, the percentage of inclusions in the casting is also reduced. The fundamental theory underlying this experiment is that the surface of the melt remains calm, in contrast to the state during rapid mixing while the degassing process. Therefore, the oxides present on the surface could not be mixed into the melt. However, the author was unable to consider the energy, cost, temporal and environmental consequences that would occur with this method of smelting. Other authors [8] researched and predicted the role of solid and gaseous reagents in the removal of inclusions, gases and magnesium in aluminium alloys, as well as slags formed during the melting process. In addition, a thermodynamic analysis of the smelting of aluminium was carried out.

Before choosing the composition of the flux, it is necessary to consider the functions, properties of the flux and the temperature that must be applied to activate the processes. In addition, you should consider the alloy in which it is added and the environmental effect of its use. Sodium or fluoride fluxes should not be included in aluminium-magnesium alloys. From a thermodynamic point of view, fluorine salts are more stable than chlorides, sulfides, and oxides. Consequently, fluoride salts added to a mixture of chlorine and magnesium would stabilize the magnesium present in the salt state. When using C₂Cl₆ tablets, a melt bubbling effect is created, in which AlCl₃ gas bubbles are generated, into which the hydrogen present in the melt diffuses. In addition, salt fluxes are also present that wet the oxide inclusions, thus removing the hydrogen trapped in the inclusions.

The authors [6] studied the effect of the C₂Cl₆ using, as well as fluxes of fluorides and chlorides on the environment in the refining of aluminium alloy, with particular emphasis on the emission of organochlorine compounds into the atmosphere. The analysis is presented in figure 1 and figure 2.

Below are shown emissions of octachlorostyrene (OCS), hexachloroethane (HCE), hexachlorobenzene (HCB), carbon monoxide (CO), total hydrocarbons (THC) and hydrogen chloride (HCl).

![Figure 1. Emissions of octachlorostyrene (OCS), hexachloroethane (HCE) and hexachlorobenzene.](image1)

![Figure 2. Emissions of oxide (CO), sum of hydrocarbons (THC) and hydrogen chloride (HCl).](image2)

The dominant trend in the development of aluminium producing corporations is the implementation of a binary vertically integrated scheme that combines aluminium smelting and recycling in parallel divisions [9]. The aspects described above indicate that in order to improve the working conditions of the smelting shop and increase the environmental efficiency of the process, products producing
environmentally unsafe gases and solid-state toxic slags, namely components containing fluorides and chlorides of alkali and alkaline earth metals, should be excluded from refining technologies.

Theoretical studies have shown that promising searches for flux compositions using oxide melts (oxides of boron, sodium, silicon, potassium, etc.) that can dissolve significant amounts of $\text{Al}_2\text{O}_3$, as well as basalt, can significantly reduce the release of harmful emissions from the processing of aluminium melts, and Carbonates are promising as degassing compounds [10].

A significant proportion of scrap aluminium alloys on the market for recycled aluminium raw materials are metallized waste with paint coatings. Parameters for remelting such scrap with traditional salt fluxes have been described in a number of papers [11, 12]. So far, there are no researches has been carried out on the remelting of such scrap using more environmentally friendly refining reagents. In the course of the experiments, three melts of aluminium scrap in the form of finely ground cans were carried out. The following describes the experiments.

Initially weighed charge materials containing 1 kg of finely divided waste aluminium packaging for beverages (figure 3).

For the qualitative determination of the quantity of crushed cans used scales with a scale from 5 g to 1000 g, and an error of 0.1 g. The crushed scrap was pressed using a hand press. The charge was loaded into a graphite crucible and placed in a triplex chamber of the melting complex of the Mining University (figure 4). Melting was carried out at a temperature of 750°C. When the temperature of the furnace on a thermocouple reached 680°C, boron oxide $\text{B}_2\text{O}_3$ was scattered on the surface of the melt in an amount of 2 g. Then the temperature was raised to 750°C. Next, a degassing refining reagent in the form of calcium carbonate was introduced into the melt using an immersion bell packed in aluminium foil in an amount of 0.2 g, previously ground to the required fraction 50-60 microns. The result of the interaction of molten aluminium and calcium carbonate under the experimental conditions is the reaction $\text{CaCO}_3 + \text{Al} \rightarrow \text{CaO} + \text{Al}_2\text{O}_3 + \text{CO}$. The change in the isobaric-isothermal potential of this reaction is shown in figure 5.

The degassing process continued at a temperature of 750°C and a pressure of 101 kPa for 3 minutes until the completion of the refining reaction, which is accompanied by intensive drilling of the melt. After that, slag consisting of $\text{B}_2\text{O}_3$ flux with non-metallic and oxide inclusions dissolved in it was collected from the melt surface. Then the melt was poured into molds. In the process, no harmful odors, emissions in the form of chlorides and fluorides were released. The alloy was cast in a round shape, and after cooling was weighed to calculate the yield of usable metal.

The yield of the metal after melting was varied from to 83.4% to 87.6% (melting No. 1 - 83.4% of the melting No. 2 – 85.7% and casting number 3 – 87.6%).
Figure 5. The dependence of the Gibbs energy of the reaction of CaCO$_3$ + Al $\rightarrow$ CaO + Al$_2$O$_3$ + CO on the temperature at the depth of immersion of a portion of calcium carbonate in an aluminium melt of 2.5 cm.

To determine the exact chemical composition of individual samples of castings 1, 2 and 3 after melting and casting of aluminium in the form selected for the required spectrometric analysis sections. The SPECTROLAB device, manufactured by Spectro, optical emission spectrometer, in which special CCD detectors are used to detect the light of spectral lines of individual elements, was used in the work. Overall was 27 analyzed elements in individual samples. The results of the analysis of individual samples of castings №1, 2 and 3 are presented in the following tables.

Table 1. The chemical composition of casting №1.

| Element | Si  | Fe  | Cu  | Mn  | Mg  | Cr  | Ni  | Zn  | Ti  |
|---------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Mass perc., % | 0.337 | 0.90 | 0.094 | 0.452 | 0.67 | 0.043 | 0.156 | 0.264 | 0.026 |

Table 2. The chemical composition of casting №2.

| Element | Si  | Fe  | Cu  | Mn  | Mg  | Cr  | Ni  | Zn  | Ti  |
|---------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Mass perc., % | 0.307 | 0.48 | 0.085 | 0.606 | 0.004 | 0.009 | 0.003 | 0.132 | 0.027 |

| Element | Ag  | B   | Be  | Bi  | Ca  | Cd  | Co  | Ga  | Li  |
|---------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Mass perc., % | 0.026 | 0.03 | 0.0007 | >0.03 | >0.012 | 0.02 | >0.05 | >0.042 | >0.0004 |

| Element | Na  | P   | Pb  | Sb  | Sn  | Sr  | V   | Zr  | Al  |
|---------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Mass perc., % | >0.02 | >0.0084 | >0.048 | <0.002 | >0.06 | >0.0085 | 0.05 | >0.036 | 96.3 |

| Element | Ag  | B   | Be  | Bi  | Ca  | Cd  | Co  | Ga  | Li  |
|---------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Mass perc., % | <0.0001 | 0.028 | 0.0001 | 0.0007 | <0.0000 | 0.0002 | <0.0001 | 0.0114 | <0.0000 |

| Element | Na  | P   | Pb  | Sb  | Sn  | Sr  | V   | Zr  | Al  |
|---------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Mass perc., % | 0.0017 | 0.0038 | 0.0067 | 0.0287 | 0.0014 | <0.0001 | 0.0054 | 0.0013 | 98.3 |
Table 3. The chemical composition of casting №3.

| Element | Si   | Fe    | Cu   | Mn   | Mg   | Cr   | Ni  | Zn   | Ti   |
|---------|------|-------|------|------|------|------|-----|------|------|
| Mass perc., % | 0.341 | 0.341 | 0.098 | 0.530 | 0.72  | 0.013 | 0.00065 | 0.015 | 0.021 |

| Element | Ag  | B    | Be   | Bi   | Ca   | Cd   | Co  | Ga   | Li   |
|---------|-----|------|------|------|------|------|-----|------|------|
| Mass perc., % | <0.0001 | 0.03  | 0.0004 | >0.001 | 0.002 | 0.001 | 0.0005 | >0.016 | 0.0001 |

| Element | Na  | P    | Pb   | Sb   | Sn   | Sr   | V   | Zr   | Al   |
|---------|-----|------|------|------|------|------|-----|------|------|
| Mass perc., % | 0.0029 | 0.0025 | 0.0039 | <0.002 | <0.001 | <0.0001 | 0.01  | 0.0026 | 97.9 |

All the studied castings are similar in composition to the AlMn1 alloy (EN AW 3103 or EN AW 3003) with a Mn content of 0.452 - 0.606%. The content of the main impurities is in the range: 0.341 and 0.90% for Fe, 0.307% and 0.341% for Si and 0.015 and 0.264% for Zn. The aluminium content varies from 96.3% to 97.9%.

The density of the alloy after refining treatment was \( \rho = 2440 \, \text{kg} / \text{m}^3 \). After the experiments, 3 additional heats were made with the sequence, as described above, but without refining treatment. The density of the alloy in these castings was \( \rho = 2270 \, \text{kg} / \text{m}^3 \). The increased density of castings after refining treatment indicates the effectiveness of the degassing effect of using calcium carbonate as a refining agent and parallel use of the flux in the form of boron oxide. During refining, intense boiling occurred, while mixing of unfavorable inclusions and re-saturation with gases hampered the presence of a liquid B2O3 flux on the surface of the melt. In the process of remelting, 4th hazard class gases were emitted in the form of CO2 gas and slag oxide components were produced in the form of B2O3·Me2O3 complexes, which are less harmful to the environment compared to slags consisting of alkali and alkaline-earth chlorides and fluorides metals. Thus, we can conclude about the effectiveness and comparative ecological purity of melting metallized aluminium wastes with the combined use of reagents of calcium carbonate and boron oxide.

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