Effective Materials from Recycled Aluminum Waste for Steel Ladle Treatment

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Abstract. The paper presents the results of research on the use of recycled aluminum waste (RAW) for steel ladle treatment. It has been established that simultaneously with the deoxidation of refining slags before desulfurization of steel, their liquid mobility increases, which eliminates the need for using fluorspar for these purposes. A thermodynamic analysis of possible reactions of formation of aluminates and calcium aluminosilicates in the refining slag has been carried out. The composition of briquettes based on RAW for liquefaction of refining slags is proposed.

To obtain high-quality steel at metallurgical plants, steel ladle treatment is carried out, which provides the required chemical composition, melt temperature, and a decrease in the number of non-metallic inclusions. An analysis of the dynamics of changes in requirements for the content of impurities in steels shows that from 1970 to 2010 the permissible sulfur concentration decreased significantly (from 0.03% to 0.003%), and for A-class steel, even more strict limits were set (0.002%). According to forecasts, by 2020, the steel pollution of this class with sulfur should not exceed 0.0015% [1]. Since 2014, for the pipes and fittings, the normative and technical documentation of Gazprom reflects the acceptable pollution standards for sulfide, oxide and silicate inclusions according to the average and maximum scores [2].

Researchers note the great potential for processing steel in the ladle using active refining slags. However, the thermodynamic and kinetic abilities of such a refining are used only by 10-12%. The efficiency of steel refining is influenced by the chemical composition of the slag, its sulfide capacity, slag oxidation, temperature treatment conditions, slag viscosity and process hydrodynamics [3].

The refining ability of slags mostly depends on their liquid mobility, since desulphurization and deoxidation processes develop at the slag-melt boundary. Most enterprises use fluorite (fluorspar) CaF2 in order to liquefy slag [4], but it is an environmentally hazardous substance, has a high cost and damages the lining of a steel-teeming ladle.

When conducting experimental melts at the Belarus Steel Works using aluminum deoxidizing agents obtained on the basis of recycled aluminum waste, it was found that aluminum deoxidizing agents positively affect the degree of steel desulphurization and the liquid mobility of the refining slag of the ladle furnace.
The addition of aluminum deoxidizing agents in an amount of 100 kg (or so) ensured an increase in slag mobility, as in the case of slag processing using both CaF₂ and deoxidizing agents.

The authors of [4] also note the positive effect of Al₂O₃ on slag liquefaction and increase the durability of the lining of the steel-teeming ladle. They also recommend to use Rantal 50GR alumina-containing material (produced by RANTAL, St. Petersburg), alumina-containing briquettes (produced by ROIS, Yekaterinburg) and slag-forming material MShA Frado-1.

Thus, introducing additives containing CaO and Al₂O₃ into the refining slags, one can control the basicity and liquid mobility of the slag, as well as eliminate the need to use fluorspar (CaF₂) [4-6]. It has been established that the content of 20–25% of Al₂O₃ in slags eliminates the need for fluorspar to liquefy them. It should also be considered that aluminates with a high content of calcium (C₃A, C₅A₃) have a higher ability to absorb CaS than aluminates with a high content of alumina (CA, CA₂). In this case, the solubility of CaS significantly depends on temperature [7].

To assess the potential possibility of reactions between Al₂O₃ and the components of refining slag to form calcium aluminates and aluminosilicates, the Gibbs energy delta (change) was calculated for 16 reactions in the temperature range of 400–1873 K [5, 6]

1) $\frac{4}{3} \cdot 3\text{CaO} \cdot \text{Al}_2\text{O}_3 + \text{Al}_2\text{O}_3 = \frac{1}{3} \cdot 12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$
2) $12\text{CaO} + \text{Al}_2\text{O}_3 = \frac{1}{7} \cdot 12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$
3) $3\text{CaO} + \text{Al}_2\text{O}_3 = 3\text{CaO} \cdot \text{Al}_2\text{O}_3$
4) $\text{CaO} + \text{Al}_2\text{O}_3 = \text{CaO} \cdot \text{Al}_2\text{O}_3$
5) $\frac{1}{2} \cdot 3\text{CaO} \cdot \text{Al}_2\text{O}_3 + \text{Al}_2\text{O}_3 = (3/2) \cdot \text{CaO} \cdot \text{Al}_2\text{O}_3$
6) $\text{CaO} \cdot \text{Al}_2\text{O}_3 + \text{Al}_2\text{O}_3 = \text{CaO} \cdot 2\text{Al}_2\text{O}_3$
7) $(1/5) \cdot 3\text{CaO} \cdot \text{Al}_2\text{O}_3 + \text{Al}_2\text{O}_3 = (3/5) \cdot \text{CaO} \cdot 2\text{Al}_2\text{O}_3$
8) $\text{CaO} \cdot \text{Al}_2\text{O}_3 + \text{Al}_2\text{O}_3 = \text{CaO} \cdot 2\text{Al}_2\text{O}_3$
9) $(1/5) \cdot 12\text{CaO} \cdot 7\text{Al}_2\text{O}_3 + \text{Al}_2\text{O}_3 = (12/5) \cdot \text{CaO} \cdot \text{Al}_2\text{O}_3$
10) $(1/5) \cdot 12\text{CaO} \cdot 7\text{Al}_2\text{O}_3 + \text{Al}_2\text{O}_3 = (12/5) \cdot \text{CaO} \cdot \text{Al}_2\text{O}_3$
11) $\text{Al}_2\text{O}_3 + 2\text{CaO} + \text{SiO}_2 = 2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$
12) $\text{Al}_2\text{O}_3 + \text{CaO} + \text{SiO}_2 = \text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$
13) $1/3\cdot \text{Al}_2\text{O}_3 + \text{CaO} + \text{SiO}_2 = (1/3) \cdot 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$
14) $\text{Al}_2\text{O}_3 + 2\text{CaO} + \text{SiO}_2 = 2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$
15) $1/2\text{Al}_2\text{O}_3 + 1/2\text{CaO} + \text{SiO}_2 = (1/2) \cdot \text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$
16) $\text{CaO} \cdot \text{SiO}_2 + \text{CaO} \cdot \text{Al}_2\text{O}_3 = 2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$

Figures 1 and 2 show the Gibbs energy delta (change) of these reactions at a temperature of 1873 K. From the presented calculations it is clear that it is theoretically possible for all 16 reactions to occur due to negative $\Delta G_t$ values. However, it should be noted that as a result of reactions' behavior, fairly high-melting compounds are formed: $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ ($t_{\text{melt}}=1535^\circ\text{C}$); $\text{CaO} \cdot \text{Al}_2\text{O}_3$ ($t_{\text{melt}}=1610^\circ\text{C}$); $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ ($t_{\text{melt}}=1572^\circ\text{C}$) [5, 8]. Considering that refining slags are multicomponent, it is also possible to form the $4\text{MgO} \cdot 5\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ($t_{\text{melt}}=1475^\circ\text{C}$) compound. Therefore, the effect of increasing the liquid mobility of refining slags with the addition of Al₂O₃ should obviously be associated with the possibility of the formation of low-melting eutectics.

Thus, eutectics with melting points of 1170, 1265, 1310, 1345, 1335 °C are formed in the CaO – Al₂O₃ – SiO₂ system [5, 8].

For the MgO – CaO – Al₂O₃ – SiO₂ system, three eutectics with low melting points can be indicated [8]:
- 5 % MgO–48.8 % CaO–41.5 % Al₂O₃–5 % SiO₂ ($t_{\text{melt}}=1295^\circ\text{C}$); 5 % MgO–48.8 % CaO–41.5 % Al₂O₃–5 % SiO₂ ($t_{\text{melt}}=1295^\circ\text{C}$); 5 % MgO–48.8 % CaO–41.5 % Al₂O₃–5 % SiO₂ ($t_{\text{melt}}=1295^\circ\text{C}$); 5 % MgO–48.8 % CaO–41.5 % Al₂O₃–5 % SiO₂ ($t_{\text{melt}}=1295^\circ\text{C}$); 5 % MgO–48.8 % CaO–41.5 % Al₂O₃–5 % SiO₂ ($t_{\text{melt}}=1295^\circ\text{C}$).
Figure 1. Gibbs energy delta (change) of reactions of calcium aluminates formation at a temperature of 1873 K (reactions 1-10).

Figure 2. Gibbs energy delta (change) of reactions of calcium aluminosilicates formation at a temperature of 1873 K (reactions 11-16).
Eutectics with melting points of 1355 and 1365 °C are also formed in the MgO – Al₂O₃ – SiO₂ system [8].

The adjustment of Al₂O₃ content in the composition of refining slags in order to liquefy them can be carried out using recycled aluminum waste [5].

For the production of an experimental batch of a refining slags thinner, recycled aluminum waste stored at an open storage area of NPF Metallon were selected [9]. In order to separate the prills of aluminum, aluminum wastes were sieved through a sieve with square holes (with a side of 5.6 mm and a diagonal of the hole of about 8 mm).

Samples were taken from the obtained screenings of the different horizons for a detailed chemical analysis, which was carried out at the testing center of the Institute of Powder Metallurgy of the National Academy of Sciences in Belarus. Screening of recycled aluminum waste contains alumina (as the main component), a small amount of magnesium oxides, silicon and iron. Subsequent analysis showed that the content of the 0-3 mm fraction in the screening is 78-80%. This fraction is of the greatest interest for the production of high-alumina fluxes and the liquefaction of ladle slags in steel production.

To separate the aluminum prills from the screened slag, it was subjected to vortex separation using a conveyor belt with a multi-pole magnetic rotor. During the rotation of a multi-pole magnetic system, vortex currents were induced in metal particles, which, in turn, created a magnetic field opposite in direction to the rotor magnetic system. As a result of the interaction of magnetic fields, metal particles contained in the screened slag were removed from the stream and separated from the non-conductive fraction [9].

For production tests, an experimental batch of a thinner in the form of briquettes based on recycled aluminum waste with the addition of 40% CaO and a binding substance was made. Briquettes were obtained using a roller press. Data on the chemical composition and distribution coefficient of sulfur of refining slag before and after the addition of a thinner are shown in table 1.

| Slag characteristics       | Slag’s chemical composition (mass fraction of oxides), % | Sulfur distribution coefficient \((L_s)\) |
|---------------------------|-------------------------------------------------------|-------------------------------------|
| Refining (initial)        | CaO: 46.5, SiO₂: 24.4, MgO: 9.8, Al₂O₃: 12.6, FeO: 2.6 | 123.4                               |
| Refining (after the thinner is added) | CaO: 52.7, SiO₂: 19.3, MgO: 8.7, Al₂O₃: 18.4, FeO: 0.9 | 146.2                               |

From table 1 it is seen that the thinning additives lead to an increase in the content of CaO and Al₂O₃ in the slag, with a noticeable decrease in iron oxides, apparently due to the content of metal aluminum prills in the additive. It should also be noted that the sulfur distribution coefficient increased from 123.4 to 146.2, which indicates the best desulfurizing ability of slag.

The addition of briquettes to the surface of the refining slag of a 100-ton steel-teeming ladle in an amount of 250 kg also provided a noticeable liquefaction of slag, which is confirmed by an increase in the mass of slag in the immersion viscometer by 70% compared to the refining slag of the initial state.

The variety of waste aluminum alloys to be processed requires careful preliminary preparation and sorting in order to obtain products with high added value. The most common wastes from aluminum and its alloys contain oiled paper, heat-insulating foam, plastic, ceramics and glass. With the introduction of compulsory sorting of household waste, the share of scrap and aluminum waste of grade 4 (class G) including bottle caps, vodka dispensers, metal cans for drinks, for the production of which food-grade aluminum alloys are used, has increased.

For the processing of such wastes, a scheme for their preparation and melting was proposed, with the production of aluminum granules using the "dry" technology.
At the first stage of preparation, recycled aluminum wastes were processed in a hammermill for glass breaking. Subsequently, the polymer-metal concentrate underwent magnetic separation in the unit with permanent magnets and the sorted magnetic component was used as part of the furnace-charge in the production of pig deoxidizing agent. The non-magnetic part of the waste was sent to a shredder for grinding to a fraction of 10-15 mm, which was subsequently subjected to magnetic and vortex separation. Using the vortex separation, a non-magnetic metal fraction was extracted, which is further used as a component of the furnace-charge during melting in a short-flame rotary furnace. The non-metallic fraction, consisting predominantly of plastic, was subject to processing to produce granules of recycled plastic sold to customers.

After the crushed and refined aluminum was melted in the short-flame rotary furnace, the melt was poured into a KROWNOMATIC dosing furnace, where it was kept at a temperature of 740-760 °C for three hours, and then the metal was fed through a heated tray to the CENTAUR unit to obtain aluminum granules using “dry” technology.

Using such schemes for the preparation of recycled aluminum waste, an experimental batch of aluminum granules AB87 (weighting 5 tons) was manufactured using dry technology and delivered to the Moldova Steel Works for production tests. The granules were predominantly spherical in shape and loaded into the silo of the ASIS injection unit.

Aluminum granules were injected into a stream of metal at the time of release from EAF in accordance with the requirements of current technology. Experimental granules were used instead of crushed aluminum in the production of a low-carbon steel with a consumption coefficient of 0.96 relative to the norm for the material used.

The obtained technological indicators of steel ladle treatment for check and experimental melts had close values both in the specific consumption of pure aluminum delivered to the steel ladle with deoxidizers and in the content of carbon, silicon, aluminum, and sulfur in continuously cast billets.

Conclusions

Thus, non-waste technology for the processing of oxidized aluminum waste makes it possible to obtain effective materials for steel ladle treatment in the form of aluminum ingots, pyramids, granules, deoxidizing mixtures and refiners for refining slag. By doing so, it is possible to provide the necessary liquid mobility of refining slag and increase its desulphurizing ability, reduce the impact on the environment, eliminating the use of CaF₂ and the disposal of waste slag and, as a result, obtain significant environmental economic and environmental effect.

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