Refinement of aluminum from sodium with graphitized materials

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Abstract. Purification of primary aluminum from sodium has been made by filtering of the melts through inert filters made of grafitized materials. Aluminum A85 and A7 was filtered under vacuum by gravity when poured from ladle to ladle. Purification decreased the content of sodium by an order. The stability of filtering materials was satisfactory. A possible mechanism of sodium removal from liquid aluminum is discussed.

Introduction
Primary aluminum produced at plants contains from 0.003 to 0.010 wt. % of sodium. Sodium spoils the properties of aluminum and its alloys and increases the content of hydrogen (table 1). To meet modern requirements on sodium content, metal should be additionally purified.

Table 1. The interrelation between content of sodium and hydrogen and cold rolling force values (Rf) [1].

| Na content, $10^{-4}$ wt.% | H$_2$ content, $10^{-4}$ wt.% | R$_f$, N/mm$^2$ |
|---------------------------|-------------------------------|----------------|
| <1                        | 0.20                          | 350            |
| 5                         | 0.40                          | 370            |
| 30                        | 0.52                          | 485            |
| 82                        | 0.48                          | 630            |

Upon plastic treatment of aluminum containing enhanced amounts of sodium, foil wastes increase considerably owing to rejects and corrosion stability of aluminum decreases substantially. According to the phase diagram of Al–Na, sodium may be in the liquid aluminum matrix in a mononuclear form [2]. At the monotectic temperature 659°C, the solubility of sodium is 0.15 and 0.0025 wt. % in liquid and solid aluminum respectively. Primary aluminum also contains a certain amount of silicon, which considerably reduces the miscibility gap in the Al–Na system. Accordingly, ternary phases are not formed in the Al–Si–Na system, but in NaSi$_2$ compound almost half of sodium atoms may be replaced by aluminum. Phases formed in this case may be assigned to a series of compounds from (NaAl)$_2$Si$_2$ to NaSi$_4$Al [2].

A variety of aluminum melts refinement methods are known. In zone melting, the coefficient of sodium distribution between solid and liquid aluminum is practically equal to 1. Upon passing through 10 zones, the content of sodium decreases from 0.024 to 0.020 wt.%, which was explained by its evaporation in high vacuum [3]. The content of sodium decreases in all cases of refinement of
aluminum melts. Previously the hexachloroethane (or others halogen-containing gases) blow was considered the most efficient method of refinement. However this process contaminates the environment and was forbidden in Europe since 1998. Instead of chemical processing of aluminum melt with gases, an active search for other methods, such as inert gas blow, filtering through active and neutral filters, application of fluxes, thermal processing in vacuum, centrifugation of melt etc., is under way at present. In this work, we have studied the application of carbon materials (fabrics and felts). Felts have low density (about 0.1 g/sm$^3$) and a very developed specific surface (300–450 m$^2$/g). Structural defects of these materials increase markedly their surface reactivity. The probability of formation of stratified intercalating compounds of sodium with carbon is high if the aluminum melt is treated with carbon materials. These compounds are supposedly formed on the surface of the filtering layer and then are displaced from the surface by aluminum atoms. As a result, sodium was transported from the bulk of the melt to the surface of capillary streams to promote evaporation of sodium and increase the efficiency of purification. As the melt temperature increases, the contribution of this effect prevailed. The developed active surface of grain-oriented fabrics and felts intensified these processes and allowed to achieve a higher degree of purification. When any other material with a diameter of pores similar to that of graphite is used the effect of aluminum melt processing intensification due to graphitized carbon materials was not observed.

**Experimental**

Fine (0.0035±0.0008 wt.% of Na) and A85 (0.0074±0.0022 wt.% of Na) primary aluminum was used. Studies were carried out in crucibles made of borosilicate graphite BSG-30 whose density is not less than 2.2 g/sm$^3$. The top crucible with a perforated bottom was covered with a grafitized material (fabrics TMP-4, TGN-2M, TMP-3 or felt VIT-1). The cell was placed in an electric resistance furnace and heated. The temperature in each fusing was 750–850°C. The fused metal was filtered under low pressure in the in-take part of the cell. The four probes were taken for analysis for sodium at each fusing: primary Al, Al melt immediately after fusion, Al melt immediately after filtration and Al upon crystallization. A high-purity graphite sampler was treated in the following manner: boiling in aqua-regia (nitrohydrochloric acid), boiling in purified water, and heating to 1000°C in vacuum. The sample of liquid metal was cooled in liquid nitrogen. Graphite fabrics and felts in various combinations and a sintered aluminum oxide filter of thickness 10 mm, porosity 85 %, and pores size 0.16 mm were tested. The content of sodium was determined by the atomic absorption method on a Perkin–Elmer spectrophotometer using standard solutions. A sample of aluminum (of mass about 1g) was washed out in extra-pure hydrochloric acid and in cleared water. Then it was dissolved in hydrochloric acid and placed in a volumetric flask (50 ml).

**Results**

The results of fusions with subsequent filtration through grafitized carbon materials and a porous plate made of sintered aluminum oxide are presented in table 2.

The content of sodium in aluminum decreased upon a filtration by a factor of 2–3 in the case of sintered aluminum oxide and by a factor of 10 in the case of grafitized carbon materials. The durability and efficiency of the filter made of grafitized carbon materials was checked by repeated filtration of aluminum through the same filter having two layers of fabric TGN-2M (see table 3).

The filter did not lower its qualities upon 10 filtrations when primary (P) aluminum was loaded and filtered (F) aluminum was obtained each time. Purification efficiency at each operation was 8.7–10.3 (N). From these tests it is also possible to conclude that the stability of the above-mentioned materials is rather high. To reduce the content of sodium in primary aluminum, filtration of the melt through a grafitized fabric, such as TGN-2M, can be recommended. Filtration also reduced the content of suspended particles in the melt and entrapped the oxide films enriched with impurities as well as large particles of intermetallic compounds.
Table 2. Experimental data on the content of sodium in aluminum upon filtration through grafitized carbon materials and a porous aluminous plate.

| Material of filter | Na content, wt. % |
|--------------------|------------------|
|                    | Primary Al | Filtered Al |
| TMP-4              | 0.0075 ± 0.0022 | 0.0028 ± 0.0008 |
| TGN-2M (2 layers)  | 0.0077 ± 0.0023 | 0.0040 ± 0.0015 |
| TMP-3              | 0.0078 ± 0.0023 | 0.0038 ± 0.0011 |
| Felt VIT-1         | 0.0073 ± 0.0022 | 0.0034 ± 0.0010 |
| TGN-2M             | 0.0067 ± 0.0020 | 0.0036 ± 0.0011 |
| Al₂O₃ plate        | 0.0074 ± 0.0022 | 0.0032 ± 0.0009 |

Table 3. Purification of the A85 aluminum from sodium by filtering through two layers of the TGN-2M fabric as a function of the number of filtrations.

| Characteristic | Number of filtrations |
|---------------|-----------------------|
|               | 1 2 3 4 5 6 7 8 9 10 |
| P, 10⁻³       | 3.8 4.0 3.5 3.0 3.7 3.4 3.1 3.6 3.7 3.3 |
| F, 10⁻⁴       | 4.0 4.4 3.7 2.9 4.1 3.3 3.5 3.7 3.9 3.8 |
| N             | 9.5 9.1 9.4 10.3 9.0 10.3 8.8 9.7 9.5 8.7 |

A ladle-to-ladle filtration through a pig-iron cell lined with a grafitized fabric TGN-2M with a working area 240 mm in diameter was carried out at the Bogoslovsky aluminum factory. The cell was equipped with a nichrome heater providing preliminary heating to 700°C. Aluminum A7 in an amount of 1700 kg was filtered by gravity. The initial content of sodium was 0.0094 wt.%, and the final concentration was 0.0020 wt.%. The temperature of primary aluminum in the ladle was 850°C. The average decrease of the content of sodium in subsequent operations was 55–79 %.

Hence, grafitized carbon materials reduce the content of sodium in primary aluminum considerably and the technology of purification is very simple and can be easily used in industry.

References
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