Refining of Primary Aluminum from Vanadium

Petr O. Bykov[1,a*], Almaz B. Kuandykov[1,b] and Ablay K. Zhunusov[1,c]

[1]Toraighyrov University, Pavlodar, Kazakhstan

[a]bykov_petr@mail.ru, [b]azeka200892@mail.ru, [c]zhunusov_ab@mail.ru

Keywords: aluminum; metallic impurities; refining; vanadium; flux.

Abstract. The paper investigates the technology of refining primary aluminum from vanadium impurities, based on flux treatment with boron-containing fluxes.

In the Pavlodar region of the Republic of Kazakhstan, on the basis of local enterprises, the production of primary aluminum and products based on local raw materials is developing.

The main problem in the production of primary aluminum on the basis of JSC "Kazakhstan Electrolysis Plant" is the presence of undesirable vanadium impurities, which pass into metal during electrolysis from baked anodes based on calcined coke (vanadium content up to 800 ppm) of the local enterprise LLP UPNK-PV (Pavlodar, Kazakhstan).

The authors investigated the process of ladle refining of aluminum from vanadium using the Al-B (3% B) alloy.

Laboratory and industrial tests have shown a decrease in the vanadium content by an average of 78% in the bulk of the metal, with an increase in its content in volume up to 5-10% of the ladle capacity. It was found that mixing leads to a certain averaging of the vanadium content in the ladle volume.

Introduction

In the Pavlodar region of the Republic of Kazakhstan on the basis of JSC "Aluminum of Kazakhstan" and JSC "Kazakhstan Electrolysis Plant", an aluminum cluster is developing, the further development of which is associated with local enterprises LLP Kazenergokabel, LLP Gissenhaus, LLP Vector-Pavlodar, LLP SNN, Producing aluminum wire rod and wire, alloyed aluminum, cast wheel disks, cast batteries, as well as by enterprises supplying raw materials for the needs of the electrolysis production of LLP UPNK-PV (production of calcined petroleum coke), etc.

Much attention in the industry is paid to improving the quality of the metal, primarily in terms of unwanted impurities. The issues of refining aluminum and its alloys have been studied in the world for a long time and remain relevant today in connection with the constantly increasing requirements for the mechanical and operational properties of products [1 - 8]. All aluminum melts have certain impurities that affect the physical and chemical properties. The main ones are hydrogen, sodium, lithium, calcium, oxides $Al_2O_3{\cdot}MgO$, spinel $Al_2O_3{\cdot}MgO$, titride A1N, silicate $CaSiO_3$, aluminate $CaA1_2O_4$, carbides SiC, TiC, $A1_4C$, intermetallic compounds Al_3Ti, Al_3Zr, AlTiZr, for the removal of which various refining methods have been successfully introduced into production [1 - 10].

The main problem in the production of primary aluminum on the basis of JSC "Kazakhstan Electrolysis Plant" is the presence of undesirable impurities of vanadium, which pass into metal during electrolysis from baked anodes based on calcined coke (vanadium content up to 800 ppm) of the local enterprise LLP "UPNK-PV" (Pavlodar, Kazakhstan) [11]. According to the requirements of GOST 11069-2001, the amount of vanadium impurity in primary aluminum should be less than 0.02 wt. %. This problem limits the use of local raw materials in the production of baked anodes (the amount of baked coke of LLP UPNK-PV is about 50% of the total amount of coke).

A promising line of research is the use of boron-based fluxes and ligatures in the refining of aluminum to bind vanadium into an intermetallic compound and further remove it from the melt [11–20]. Industrial tests are known in a number of areas. The first option included the introduction of boric acid (H_3BO_3) into the electrolyzer (3 kg daily). This method has shown good results of refining, but a decrease in the resistance of the bottom of the cell. The second method consisted of feeding boric acid-based flux during the casting of aluminum in the casting department directly into the molds of the casting machine. This method showed a slight decrease in the vanadium content (by 4 - 6 ppm). The third option for using boron was its introduction into the composition of the anode mass during the production of baked anodes (up to 3 kg per one anode). This method also did not give tangible results in reducing the vanadium content in the finished aluminum.

Thus, solving the issue of successful removal of vanadium from aluminum melts is of great importance for the further development of the aluminum cluster in Kazakhstan.

Field Study and Results

Primary aluminum production in Kazakhstan is concentrated in the Kazakhstan Electrolysis Plant JSC, which includes an aluminum electrolysis workshop with a foundry, an anode production workshop and auxiliary workshops [15]. The annual production volume is more than 250 thousand tons of aluminum grades A7, A8, A85 (table 1).

Table 1. Aluminum grades according to GOST 11069-2001

Grade	Impurity,[%], no more									Al,[%], not less
	Si	Fe	Cu	Mn	Mg	Zn	Ga	Ti	Other impurities (each separately)	
A85	0.06	0.08	0.01	0.02	0.02	0.02	0.03	0.008	0.02	99.85
A8	0.10	0.12	0.01	0.02	0.02	0.04	0.03	0.01	0.02	99.80
A7	0.15	0.16	0.01	0.03	0.02	0.04	0.03	0.01	0.02	99.70
A7E	0.08	0.20	0.01	-	0.02	0.04	0.03	0.01	0.02	99.70

The JSC "Kazakhstan Electrolysis Plant" uses the GP-320 technology of the Chinese Institute of GAMI. The cell series is housed in two parallel electrolysis buildings with a length of about 1000 meters and consists of a total of 288 cells connected in series. The rated current of a series of electrolysers is 320–330 kA [15].

The anode production shop has four main sections: a section for the production of "green" anodes; anode warehouse; anode baking oven; anode assembly area [15].

The foundry department accepts liquid metal obtained in the electrolysis buildings and pours it into 20 kg ingots.

Approximate data on the consumption of materials by the plant are given in table 2.

Table 2. Approximate consumption of raw materials [15]

Material	Specific consumption, [kg / t]	Annual consumption, [tons / year]
Alumina	1930	482 500
Petroleum coke	0.365	91 250
Liquid coke	0.0964	24100
Aluminum fluoride	22	5500
Cryolite	1	250

For aluminum refining, fluxes of the following compositions are used [15]:

- 50% cryolite + 50% sodium chloride;
- 50% cryolite + 50% aluminum fluoride;
- 23% cryolite + 30% sodium chloride + 47% potassium chloride;
- 23% cryolite + 47% sodium chloride + 30% potassium chloride;
- carnalite flux.

The total consumption of flux is 1 - 2 kg per 1 ton of aluminum. Raw materials used for fluxes are supplied according to the following requirements [15]:

- cryolite in accordance with GOST 10561;
- aluminum fluoride according to GOST 19181;
- sodium chloride according to GOST 13830 and GOST 11314;
- potassium chloride according to GOST 4568;
- glass mesh (filter) SSF-Z, SSF-4.

The experience of using these fluxes shows the impossibility of removing vanadium from primary aluminum.

The authors carried out studies on ladle refining of raw aluminum. The chemical composition of raw aluminum is presented in table 3.

Table 3. Chemical composition of raw aluminum

Al, [%]	Si, [%]	Fe, [%]	Cu, [%]	Mn, [%]	Mg, [%]	Zn, [%]	Cr, [%]	Ti, [%]	V, [%]
98.53	0.117	1.1545	0.0186	0.0079	0.0260	0.0879	0.002	0.017	0.033

At the first stage, laboratory studies were carried out in the laboratory of the Metallurgy Department of Toraigyrov University. In an induction crucible furnace GW-MF-25, raw aluminum was remelted. At a temperature of 850 °C, Al-B ligature was introduced under the metal level at the rate of 1.2 - 2 kg / t of raw aluminum. The metal was kept for 10 - 20 minutes in an induction furnace, then poured into a ladle heated to 750 °C and settled in a muffle furnace at this temperature for 30 minutes to precipitate the formed vanadium intermetallic compounds on the bottom of the furnace. After settling, the metal was sequentially poured into three ladles to determine the vanadium content in the metal portions at the beginning, middle and end of casting. Each experiment was repeated three times.

At the end of the experiments, the chemical composition of the refined raw aluminum was measured using a DFS-500 optical emission spectrometer. The vanadium content in raw aluminum is given in table 4.

Table 4. Results of laboratory tests to remove vanadium from raw aluminum

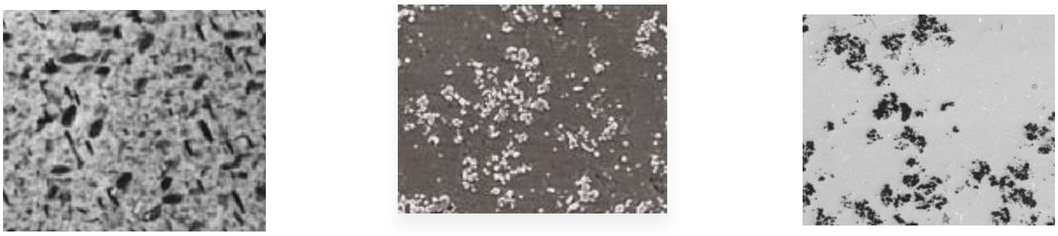
Sample number	Initial V content, [%]	Al-B, [kg / t]	Processing time and settling in a ladle, [min]	V content after experiment, [%]		
				Casting start	Middle of casting	End of casting
1	0.033	1.2	40	0.0084	0.0089	0.04
2	0.033	2.0	50	0.0072	0.0078	0.09
3	0.033	1.2	50	0.0075	0.0083	0.07
4	0.033	2.0	40	0.0073	0.0078	0.08

The work investigated the microstructure of raw aluminum before and after refining with Al-B alloy. The microstructure was assessed using a Metam-32 metallographic microscope.

In the structure of raw aluminum before processing, inclusions of intermetallic compounds VAl_3 are found (Figure 1a). In the structure of raw aluminum after processing, inclusions of intermetallic compounds VB_2 (Figure 1b), AlB (Figure 1c) and partially VAl_3.

At the second stage of work, together with the specialists of Kazakhstan Electrolysis Plant JSC, pilot tests were carried out to remove vanadium from raw aluminum with a vanadium content of 0.0210%.

The tests were carried out as follows. In an empty vacuum ladle with a capacity of 7.2 tons, Al-B ligature was loaded at the rate of 1.2 to 2 kg / t of raw aluminum. Then the vacuum ladle was fed into the electrolysis building, where aluminum was discharged from the electrolyzers. After casting, the vacuum ladle was sent to the foundry, where it settled for 1-4 hours to carry out refining and deposition of the resulting vanadium intermetallic compounds on the bottom of the ladle. Then the metal was poured into the mixer.



a) VAl_3 (×200 μm) b) VB_2 (×200 μm) c) AlB (×200 μm)

Fig. 1. Microstructure of raw aluminum before and after refining

During the overflow, metal samples were taken to determine the vanadium content in raw aluminum.

The test results are shown in table 5.

Table 5. The results of industrial tests to remove vanadium from raw aluminum

Sample number	Initial V content, [%]	Al-B, [kg / t]	Settling time in the ladle, [min]	V content after experiment, [%]		
				Casting start	Middle of casting	End of casting
1	0.0210	2	1	0.005	0.007	0.1
2	0.0210	1.2	3.5	0.003	0.004	0.1
3	0.0210	1.5	2.15	0.007	0.01	0.04
4	0.0210	1.4	2 + additional mixing	0.004	0.008	0.06

The Discussion of the Results

Calculations show that the transfer of anode production to Kazakhstan Electrolysis Plant JSC completely to LLP UPNK-PV coke will increase the supply of local calcined coke from 51.875 thousand tons to 103.750 thousand tons, which will ultimately increase the local content of raw materials in the production of domestic aluminum subject to solving problems with the removal of vanadium impurities from aluminum.

The authors investigated the process of refining aluminum from vanadium when using Al-B (3% B) ligature when it is introduced outside the electrolysis bath (into a vacuum ladle).

Laboratory and industrial tests have shown a decrease in the vanadium content by an average of 78% in the bulk of the metal, with an increase in its content in volume up to 5-10% of the ladle capacity. It has been found that mixing leads to a certain averaging of the vanadium content in the ladle volume.

From tables 4 and 5 it can be seen that the treatment of raw aluminum with Al-B ligature makes it possible to transfer a significant amount of vanadium to an intermetallic compound (on average 78%), which contributes to the further removal of vanadium from raw aluminum.

With this casting technology, an increase in the content of vanadium intermetalides in the lower part of the ladle is observed, which leads to an increase in the vanadium content in the volume up to 5-10% of the ladle capacity.

Additional mixing of raw aluminum during the settling period leads to a certain averaging of the vanadium content in the volume of the ladle, while maintaining an increased vanadium content in the final portions of the metal during pouring into the mixer.

Conclusions

1) The technology of ladle refining of raw aluminum from vanadium impurities based on Al-B ligature was experimentally investigated, which showed the possibility of reducing the vanadium content by an average of 78%.

2) Analysis of experimental data shows an increase in the content of vanadium intermetalides in the lower part of the ladle, which leads to an increase in the content of vanadium in the volume up to 5-10% of the capacity of the ladle.

3) Additional mixing of raw aluminum during the settling period leads to a certain averaging of the vanadium content in the volume of the ladle with an increased vanadium content in the final portions of the metal during pouring into the mixer.

References

[1] C. Vives, Electromagnetic refining of aluminum alloys by the CREM process: Part I. Working principle and metallurgical results, Metallurgical Transactions B. 20 (1989) 623-629.

[2] L. Zhang, D.G. Robertson, G. Jianwei, L. N. Wiredu, Removal of iron from aluminum: a review, Mineral Processing and Extractive Metallurgy Review. 33(2) (2012) 99-157.

[3] K. Al-Helal, I. Stone, Z. Y. Fan, Refinement of primary silicon crystals by novel P-Doped γ-Al_2O_3 particles in solidification of hypereutectic Al-Si alloys, Materials Science Forum. 877 (2016) 550-557.

[4] Information on: https://books.google.ru/books?id=xAykAwAAQBAJ&printsec=frontcover&dq=inauthor:%22NIIR+Board+of+Consultants+and+Engineers%22&hl=ru&sa=X&ved=2ahUKEwiN9Yzkye7uAhVjs4sKHTufCaoQ6AEwAXoECAEQAg#v=onepage&q&f=false.

[5] K. Grjotheim, C. Krohn, M. Malinovsky, K. Matiasovsky, J. Thonstad, Aluminum Electrolysis: Fundamentals of the Hall Heroult Process, second ed., Aluminium GmbH, Dusseldorf, 1982.

[6] C.J. Simensen, and G. Berg, A survey of inclusions in aluminum, Aluminium. 56(5) (1980) 335-338.

[7] I. Polmear, Light Alloys, fourth ed., Butterworth-Heinemann, 2005.

[8] V.V. Artamonov, A.O. Bykov, P.O. Bykov, V.P. Artamonov, Measurement of the tap density of metal powders, Powder Metallurgy and Metal Ceramics. 52(3-4) (2013) 237-239.

[9] K. Nakajima, O. Takeda, T. Miki, K. Matsubae, S. Nakamura, T. Nagasaka, Thermodynamic analysis of contamination by alloying elements in aluminum recycling environ, Sci. Technol. 44(14) (2010) 5594-5600.

[10] J.A. Taylor, J.F. Grandfield, A. Prasad, The impact of rising Ni and V impurity levels in smelter grade aluminium and potential control strategies, Materials Science Forum. 630 (2009) 129-136.

[11] E.S. Gorlanov, Alloying Cathodes of Aluminum Electrolyzers by the Method of Low-Temperature Synthesis of Titanium Diboride: dissertation for the degree of Doctor of Technical Sciences, St. Petersburg State University, St. Petersburg, 2020.

[12] V.I. Shpakov, V.S. Razumkin, V.G. Kokulin, E.V. Nizovtsev, V.G. Ivanov, L.P. Trifonenkov, V.M. Nikitin, RU Patent 2,084,548. (1997).

[13] E.S. Gorlanov, A.A. Batrachenko, B.S. Smailov, A.Y. Morozov, Role of vanadium in aluminum electrolyzer melts, Metallurgist. 62(9-10) (2019) 1048-1053.

[14] E.S. Gorlanov, A.A. Batrachenko, B.S. Smailov, A.P. Skvortsov, Testing baked anodes with an increased vanadium content, Metallurgist. 62(1-2) (2018) 62-69.

[15] A.T. Ibragimov, R.V. Pack, Aluminum Electrometallurgy, Kazakhstan Electrolysis Plant, Dom Pechati, Pavlodar, 2009.

[16] H.P. Sun, J. Wu, T. Tang, B. Fan, Z.H. Tang, Effect of vanadium carbide on commercial pure aluminum, International Journal of Minerals Metallurgy and Materials. 24 (2017) 833-841.

[17] S. Kumar, A. Jain, Y. Kojima, Thermodynamics and kinetics of hydrogen absorption-desorption of vanadium synthesized by aluminothermy, Journal of Thermal Analysis and Calorimetry. 130 (2017) 721-726.

[18] Q. Li, Z.W. Chen, Q. Luo, B.W. Li, Experimental investigation and thermodynamic calculation of the Al-rich corner in the ternary Al-Ti-V system, Materials & Design. 115 (2017) 339-347.

[19] A. Khaliq, M.A. Rhamdhani, G.A. Brooks, J.F. Grandfield, Removal of vanadium from molten aluminum-part I. Analysis of VB2 formation, Metallurgical and Materials Transactions B. 45 (2014) 752-768.

[20] A. Khaliq, M.A. Rhamdhani, G.A. Brooks, J.F. Grandfield, Removal of vanadium from molten aluminum-part II. Kinetic analysis and mechanism of VB2 formation, Metallurgical and Materials Transactions B. 45 (2014) 769-783.