



Study of the influence of sulfur and vanadium on the quality of produced aluminum

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ABSTRACT: The presence of sulfur and vanadium in aluminum production significantly affects the mechanical, chemical, and structural properties of the final product. Sulfur can lead to the formation of brittle phases, reducing the ductility and overall performance of aluminum alloys. Vanadium, on the other hand, influences grain refinement and mechanical strength but may introduce unwanted phase formations at higher concentrations. This study examines the impact of varying sulfur and vanadium concentrations on the microstructure, hardness, and corrosion resistance of aluminum. Experimental analyses, including spectroscopy, scanning electron microscopy (SEM), and X-ray diffraction (XRD), provide insights into the phase transformations and structural changes induced by these elements. The findings contribute to optimizing aluminum alloy compositions for improved durability and industrial applications.

KEY WORDS: Aluminum alloys, sulfur contamination, vanadium effect, mechanical properties, microstructure analysis, phase transformation, corrosion resistance.

I. INTRODUCTION

Several years ago, a steady increase in the sulfur content in the anode mass associated with a general decline in the quality of the extracted oil arose and continues to persist. An increase in the sulfur content in the involved petroleum cokes leads to a deterioration in the quality of exhaust gas purification, which leads to an increase in the environmental risks of aluminum production. The involvement of high-sulfur cokes also reduces the technical and economic indicators of aluminum production as a whole. In earlier years, studies of the effect of sulfur on the aluminum electrolysis process were practically not carried out due to the relatively low sulfur content in the involved petroleum cokes and, as a result, its small effect on the overall efficiency of the process. Longer-term, the sulfur content in the cokes that are involved will gradually build up with a gradual physical increase in consumptions of petroleum cokes: over 3-5 years more than 1.3 million tonnes/year of new aluminum production facilities will be brought into operation, which makes scientific research and practical work to optimize electrolytic aluminum production involving high-sulfur cokes relevant.

II. SIGNIFICANCE OF THE SYSTEM

As it has been reported previously, when the sulfur concentration in the petroleum coke used to prepare the electrolyte is increased, this intensifies the processes of corrosion of electrolyzer metal structures that results in an increase in iron content in produced raw material. However, the impact of sulfur variations on the anode mass develops with a delay in time. The very leakage time is linked first of all, with the quite large size of anode column: a period from loading the negative mass until it reaches a combustion zone makes up to months. Based on comparative data showing the sulfur content in the loaded anode mass, as well as changes in iron in produced raw aluminum through statistical experiment was discovered to be the correct value of time delay. The sample was taken from 10% of the electrolyzers corresponding to the lowest iron content (to limit its preponderance with respect to other factors which exerted an influence on it). The outcome of this statistical experiment is depicted in Figure 1.

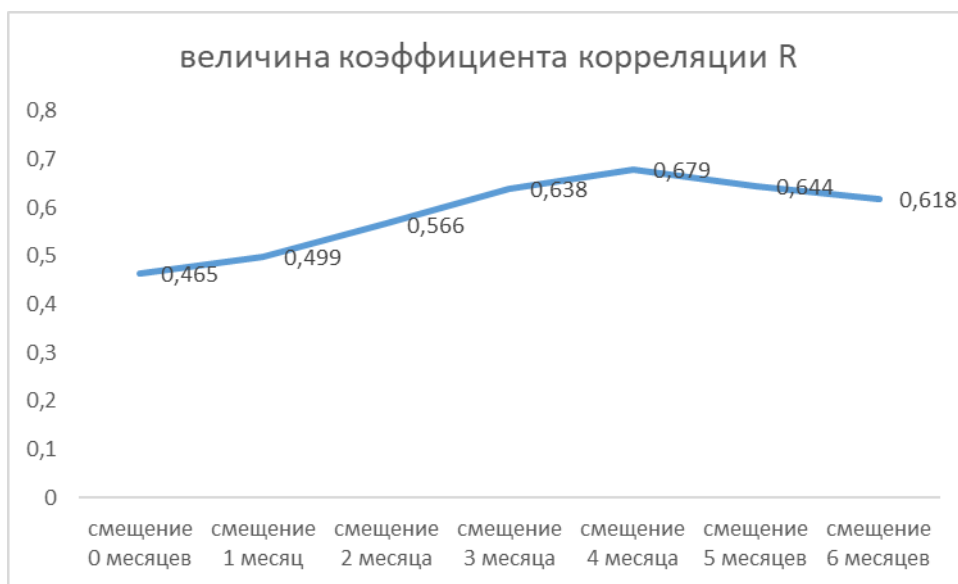


Fig. 1. Change of the correlation coefficient R value of the iron content in aluminum and sulfur content in loaded anode mass depending on displacement of general data sample

III. METHODOLOGY

Analysis of Figure 1. shows that you should take into account 4 months as the most correct value of the shift - this corresponds to the maximum of the correlation coefficient $R = 0.679$. It is the time from when the anode mass is loaded till it reaches combustion zone. Considering a certain value of the time shift determined by the anode mass influence from moment of its loading directly into the anode of the electrolyzer, statistical study of the dependence between content of iron in raw aluminum and sulfur concentration in anode mass was held. A passive statistical experiment was made to eliminate other causes of the increase in iron content, on electrolyzers leaving the first decile (10%) of a sample of all electrolyzers - with a minimum iron content. The dependence revealed is illustrated in Fig. 2.

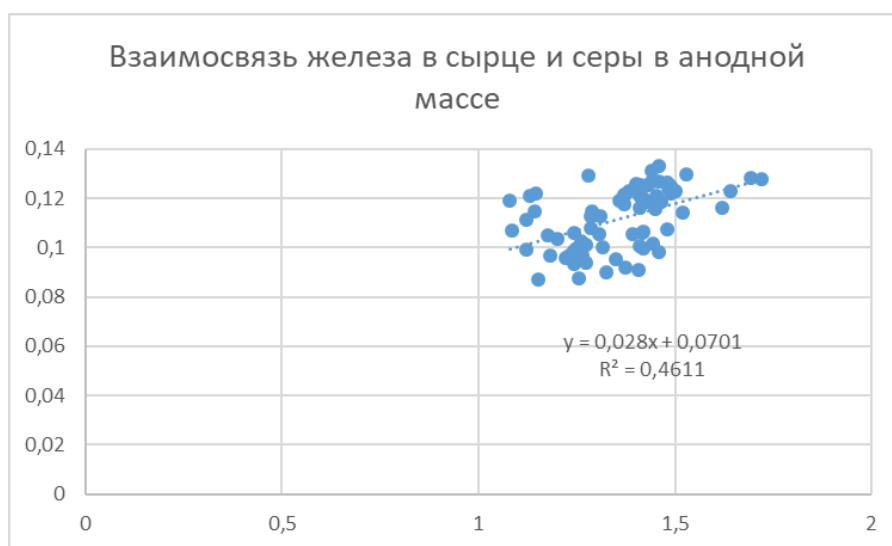


Fig. 2. 4 months time lag for the relationship of iron content with aluminum and sulfur in the anode mass

IV. EXPERIMENTAL RESULTS

The obtained dependence of the iron content in raw aluminum and sulfur in the anode mass in the form of a formula is given below (1):

$$C_{Fe} = 0,0701 + 0,028 \times C_s \tag{1}$$

where:

C_{Fe} – content of iron in the produced raw aluminum, %

0.0701 – the base (not dependent on sulfur content in anode mass) iron content in raw aluminum, %

0.028 – statistical coefficient of the sulfur concentration in the anode mass and iron content in produced raw aluminum relationship, %

C_s – anode mass sulfur content, %

Since the range of commercial products produced by the foundry department should limit the average weighted iron content in the raw material. Accordingly, if the average weighted iron content in commercial medication according to this range is 0.20%, high quality blending need necessarily that the average weighted iron content of electrolytic aluminum as required about by 0.01% lower than in commercial metal. In this program, the upper limit of average weight iron content in electrolytic aluminum is 0.19%. Therefore, by using the dependence (1) defined above, it is easy to find out by reverse calculation what would be the maximum sulfur content in anode mass:

$$C_s = \left(\frac{C_{Fe} - 0,0701}{0,028} \right) \tag{2}$$

READ MORE: Thus the maximum content of sulfur permissible in a mass anode should be calculated to 4.28%. Which, equals the sulfur value in petroleum coke $4.28/0.7 = 6.11\%$, which is higher than that of higher-sulfur coke sulfur concentration. The performance of this passive statistical experiment enabled us to obtain an empirical formula for the dependence of the quantity of electrolyzers providing high-grade metal on the average weighted sulfide content in anode mass (3):

$$N_{BC} = 100 \left(N + \left(18040 \left(0,19 - \frac{112 C_{Fe2O3} Al_2O_3 \times q_{Al_2O_3}}{160} - C_{Fe AM} \times q_{AM} - \frac{0,1}{P_1} - 0,001 - 0,028 C_{SAM} - 0,0506 \right) \right) \right) \tag{3}$$

where:

N_{BC} - Number of electrolytic cells producing raw aluminum of the highest grades, %;

N - Basic number of electrolytic cells of the highest grades, pcs;

18040 - Conversion factor showing the effect of changes in iron income on the number of electrolytic cells of the highest grades for the conditions of PJSC RUSAL Bratsk (2334 installed electrolytic cells), pcs/Fe %;

0.19 - Basic iron content in electrolytic cells of the highest grades, %;

112/160 - Stoichiometric conversion factor of the iron oxide content in alumina to the pure iron content;

$C_{Fe2O3 Al_2O_3}$ - Average weighted iron oxide content in processed alumina (including sweepings and secondary alumina), %;

$q_{Al_2O_3}$ - Alumina consumption for aluminum production, t/t;

$C_{Fe AM}$ - Average weighted physical iron content in the anode paste used, %;

q_{AM} - Anode mass consumption for aluminum production, t/t;

0.1 - Coefficient taking into account the effect of corrosion of the process tool on the iron content in the produced raw aluminum;

P_1 - Average frequency of technological treatments of electrolyzers, days;

0.01 - Correction for the presence of APG systems, %;

0.028 - Coefficient taking into account the effect of sulfur content in the anode mass (corrosion of GSK sections and anode pins);

C_{SAM} - Sulfur content in the anode mass, %;

0.0506 - Correction for melting of the flange sheet;

N_{AV} - Average number of operating electrolyzers.

Let us consider the influence of vanadium on the quality of the produced aluminum. As is known, of all the microimpurities in high-sulfur and low-sulfur cokes, only the vanadium content differs significantly. The vanadium concentration is in good agreement with the sulfur concentration in petroleum coke (correlation coefficient $R > 0.9$) – Fig. 3. This dependence is characteristic of both low-sulfur and high-sulfur cokes.:

The experimental results demonstrate that dust accumulation has a significant negative impact on the electrical performance of solar panels. The voltage-current (V-A) and power-voltage (P-V) characteristics of the panels were adversely affected, with noticeable reductions in voltage, current, and power output as dust accumulated on the surface.

The findings also highlight the importance of cleaning and maintaining solar panels in dusty environments to ensure optimal energy production.

Given the substantial impact of dust on panel performance, future work should focus on developing efficient dust removal systems, such as automated cleaning technologies, to mitigate this issue. Additionally, further research into dust-resistant coatings and materials could provide long-term solutions to improve the durability and performance of solar panels in dusty regions like Tashkent.

In conclusion, this study underscores the need for addressing the effects of dust on solar energy systems, particularly in areas prone to dust storms and pollution. By implementing proper maintenance strategies and improving panel technology, the efficiency and longevity of solar panels can be significantly enhanced, contributing to the overall success of solar energy adoption.

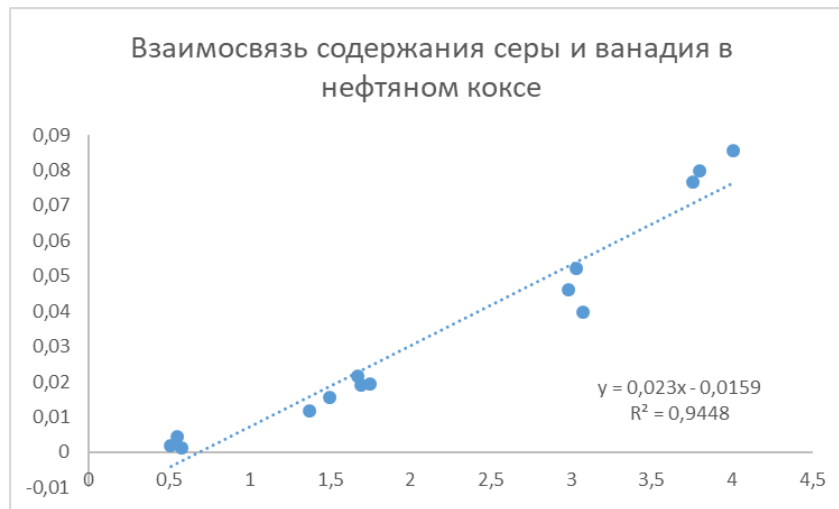


Fig. 3. Relationship between vanadium and sulfur content in petroleum coke

Vanadium, being a more electropositive element than aluminum, is almost completely concentrated in liquid aluminum.

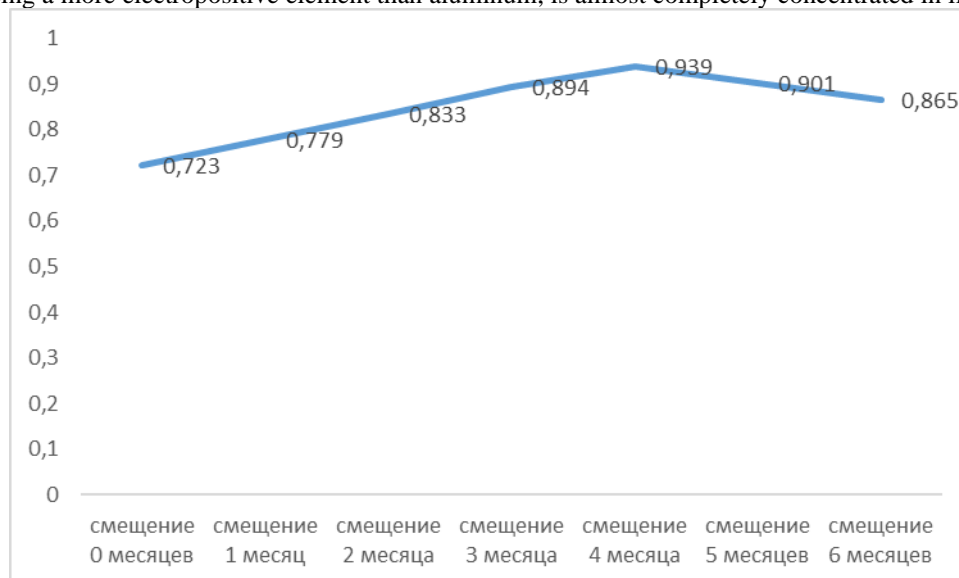


Fig. 4. Change in the value of the correlation coefficient R of the vanadium content in aluminum and the vanadium content in the loaded anode mass with a shift in the general data sample.

The correlation between the vanadium content in raw aluminum and the vanadium content in the anode mass (Fig. 4.) has the same character as the correlation between the iron content in raw aluminum and the sulfur content in the anode mass (Fig. 1.). This indicates that vanadium enters the raw aluminum from the base of the anode.

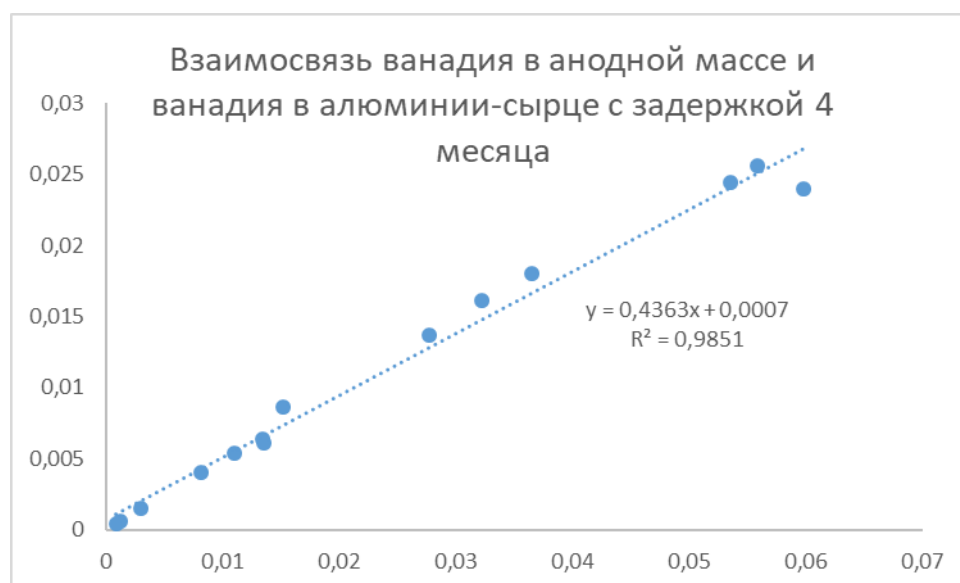


Fig. 5. Relationship between vanadium content in aluminum and vanadium content in petroleum coke with a time lag of 4 months

Taking into account the consumption coefficient of the anode mass for the production of raw aluminum and the share of petroleum coke in the anode mass, more than 94% of all vanadium in the anode mass ends up in the raw aluminum (Fig. 5.). The dependence of the vanadium content in raw aluminum on the vanadium content in the form of a formula is given below (4):

$$C_V = 0,0007 + 0,4363 \times C_{V_{AM}} \quad (4)$$

where:

C_V – vanadium content in the produced raw aluminum, %

0.0007 – base (independent of vanadium concentration in the anode mass) vanadium content in raw aluminum, %

0.4363 – statistically determined coefficient of the relationship between the vanadium concentration in the anode mass and the vanadium content in the produced raw aluminum, %

$C_{V_{AM}}$ – vanadium concentration in the anode mass, %

Vanadium is fairly easily removed from raw aluminum by boron compounds: boric acid (H_3BO_4), Al-B ligature, borax ($Na_2B_4O_7 \cdot 10H_2O$).

To assess the corrosion of the anode pins, the anode pins were weighed during operation. The corrosion loss of the anode pin is shown in Fig. 6.

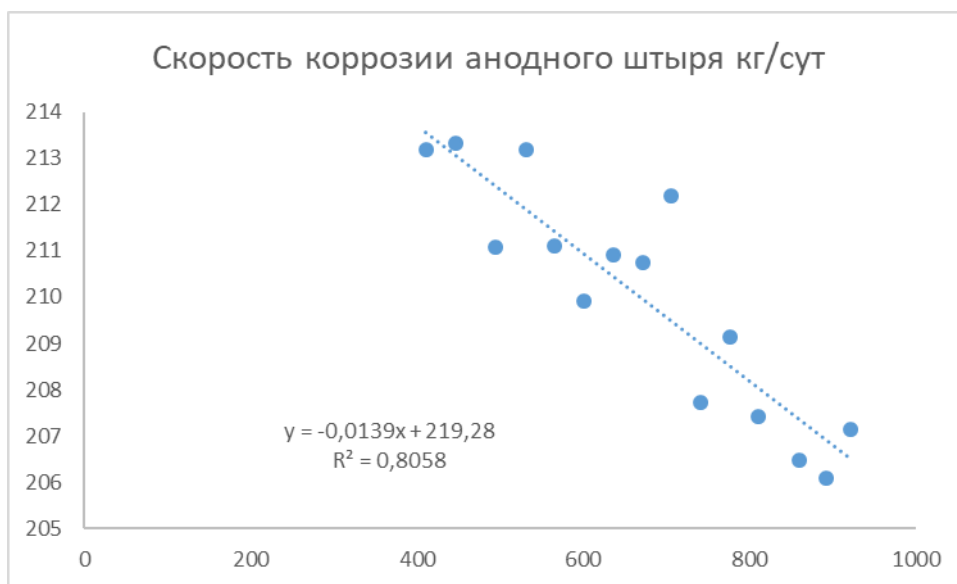


Fig. 6. Dependence of the anode pin weight on the service life

Analysis of Fig. 6. shows a good relationship between the parameters "anode pin weight" and "anode pin service life", the coefficient in the relationship equation shows that the daily loss of the anode pin weight is 0.0139 kg.

Oxidation of the anode pin occurs in the absence of oxygen in the presence of sulfur, therefore the corrosion product of the anode pin is iron sulfide (5):



The most suitable way to reduce the intensity of anode pin corrosion is to use a more electrochemically active metal. In this case, the most accessible option is to use aluminum chips, which are formed when cutting ingots in the foundry. The chips have a developed surface, so their remelting is difficult due to high burn-off. In this particular case, high burn-off is, on the contrary, a necessary requirement. Oxidation of aluminum in the absence of oxygen and the presence of sulfur will occur with the formation of aluminum sulfide (6):



With a step of rearranging the anode pins of 40 cm and, accordingly, a rearrangement cycle of 6 days, the total loss of iron in a steel pin is $13.9 \cdot 6 = 83.4$ grams of iron. According to stoichiometry, to replace this amount of iron, 26.3 grams or $26.3 / 2.7 = 97.4$ cm³ of aluminum in the form of chips pressed into a tablet are required. A tablet of pressed aluminum chips is placed in a pin hole under the heel of the pin being rearranged. The daily requirement for aluminum chips for rearranging the anode pins is 189.4 kg, which is less than the volume of daily chips generated in foundry departments - 200-220 kg. To evaluate the efficiency of using aluminum chips to reduce the corrosion of anode pins and, as a consequence, improve the quality of the produced raw aluminum, an active experiment was conducted, which consisted of rearranging the anode pins with the addition of briquetted aluminum chips during rearrangement. To determine the efficiency of rearrangement, the anode pins were weighed in pilot electrolyzers and witness electrolyzers. The results of the experiment are shown in Fig. 7.

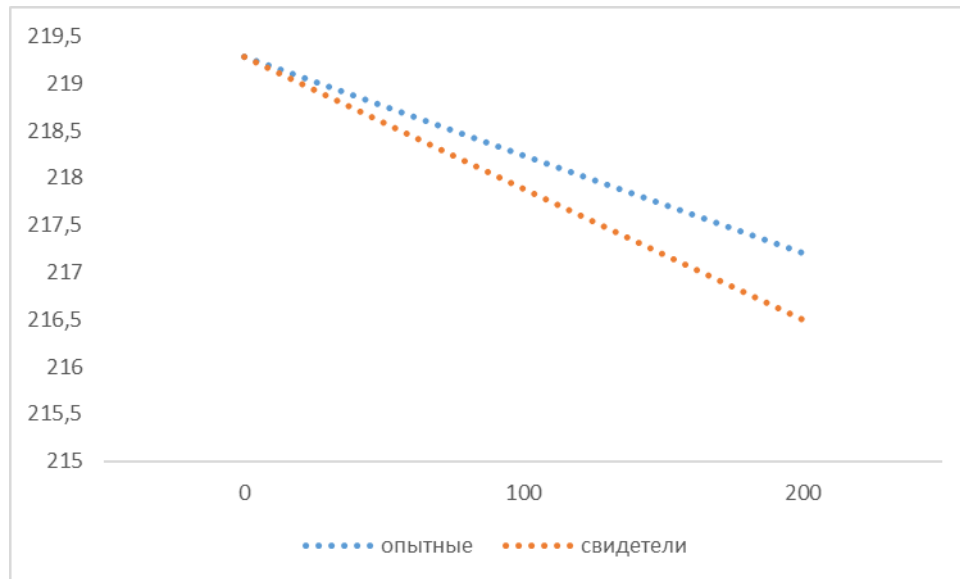


Fig. 7. Comparison of the weight loss of a group of experimental (with aluminum shavings) and a group of witness anode pins.

The use of aluminum shavings made it possible to reduce the corrosion rate of anode pins by 0.0024 kg/day.

V. CONCLUSION AND FUTURE WORK

1. The chemical composition of petroleum cokes has been studied, and it has been shown that high-sulfur cokes have a higher sulfur and vanadium content than low-sulfur cokes. The concentration of other trace impurities does not differ significantly.
2. It is shown that increasing the sulfur content intensifies the corrosion process of the electrolyzer metal structures, which leads to an increase in the iron content in the produced aluminum. The dependence of the iron content in the produced raw aluminum on the sulfur content in the anode mass is determined.
3. The behavior of vanadium in the process of electrolytic production of aluminum is studied. The dependence of the vanadium content in raw aluminum on the vanadium content in the petroleum coke used is determined.

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