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Study on gaseous impurities in α-alumina, used single crystals growing

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The optimal condition of water content determination in α-Al_2O_3, including sample mixing with methanol followed by titration of the suspension with K.Fisher reagent in the presence of methylene-blue background dye have been found. We have proved the absence of any significant systematic errors by variation of weighed. The determination limit, corresponding to standard deviation of single result 0.3, of the methodic developed is $9 \cdot 10^{-2}$ mass %. Thermogravimetric and mass-spectrometric data show that α-Al_2O_3 contains not only water, but also significant amounts of CO and CO_2, which, apparently, is the main reason of blowhole-like defects in those single crystals. We assume that material degassing by heating it in vacuum can allow a more effective elimination of such defects in the crystals, than the widely used thermal treatment of the material at atmospheric pressure.

Установлены оптимальные условия определения содержания воды в α-Al_2O_3, включающие перемешивание образца с метанолом и последующее титрование полученной суспензии реактивом К.Фишера в присутствии фонового красителя — метиленовой синей. Отсутствие значимых систематических погрешностей доказано при помощи метода варьирования навесок. Предел определения разработанной методики, соответствующий относительному стандартному отклонение единичного результата 0,3, оказался равным $9 \cdot 10^{-2}$ мас.%. По данным термогравиметрии и масс-спектрометрии установлено, что, кроме воды, α-Al_2O_3 содержит значительные количества CO и CO_2, что, по-видимому, является основной причиной появления в этих монокристаллах дефектов в виде газовых пузырей. Высказано предположение, что дегазация сырья путем его нагревания в вакууме позволит полнее устранять образование в кристаллах указанных дефектов, чем часто применяемая термообработка сырья при атмосферном давлении

Determining moisture content in powdered alumina is necessary due to its α-form use as a material for growing corundum, sapphire as well as garnets and other compound oxides single crystals. Pores and inclusions lower the operating characteristics of the grown single crystals, which makes the surface treatment more complicated and increases light scattering. The common condition of pores forming in single crystals, grown by Czochralski, Kyropoulos or Stepanov methods, is melt oversaturation with soluted gases [1] coming there from the initial material as adsorbed gaseous compounds and water. In this paper we study the potential of using K.Fisher titrimetric method with visual indication of titrating end for determining water content in alumina α-form.

We use for the titration K.Fisher reagent solution with titre 2.0–3.0 mg/ml, prepared by mixing the solutions of sulfurous anhydride in pyridine and iodine in methanol (volume ratio 1:2.17) from the standard set, made by firm RIAP (Kyiv). K.Fisher reagent titre was determined in

Table 1. Validity check of water content evaluation in Al_2O_3*

m, mg	742.5	278.9	382.6	381.7	469.4	379.5	379.4	386.6	380.3	380.3	380.9
H_2O found (C_i), mass %	2.2	2.24	2.11	2.16	2.1	2.06	2.22	2.13	2.14	2.16	2.13
$\overline{C}$, mass %	2.15										
S_r	0.02										

* C_i is H_2O content, mass %, found at batch weight m; S_r is relative standard deviation of a single result.

the day of making analyses on standard water solution in methanol. The background dye was methanol solution of methylene-blue with 1.0 mg/ml concentration. Titration was carried out in the equipment isolating the reagent and probe from the moisture in the air [2]. For water extraction from the alumina and the methylene-blue solution we used methanol, previously dried by boiling in the presence of metal calcium, then distilled.

We placed 20 ml methanol and a drop of methylene-blue solution into the titration bottle, then the bottle was attached to a burette. The solution of K.Fisher reagent was added from the burette for binding the water in methanol and on the walls of the container for titration. The solutions were stirred with magnet mixer. The color changed from blue-green to deep green with yellow hue at the end of titration. Then α-Al_2O_3 weighed portion (700–1000 mg) was placed in the same bottle, the mixture was stirred for 15 min with magnetic mixer at room temperature and the suspension was titrated with K.Fisher reagent. The result of evaluation (mass %) was calculated by formula:

$$X = V \cdot T \cdot 100/m,$$

where V is K.Fisher reagent volume, used for titration of the probe under analysis, ml, T is K.Fisher reagent titre (mg/ml), m is Al_2O_3 weight (mg).

Thermogravimetric studies were carried out with thermoanalytic system Mettler TA3000 (Switzerland). Al_2O_3 weight (9–12 mg) was placed in the furnace and the sample was heated to 220°C at 3 grad/min. Weight decrease was registered permanently.

Mass spectrometer studies were done with mass spectrometer IPDO-2. α-Al_2O_3 weight (32 g) was put into a quartz ampoule 50 mm in diameter, by attaching it to vacuum system, and after reaching the pressure $3.9 \cdot 10^2$ Pa the ampoule was put into resistance tube furnace. The temperature in the furnace was increased to 700°C at 200 grad/h, the composition of gas atmosphere in the vacuum system being controlled with mass spectrometer. The statistical treatment of results was made at confidence probability $P = 0.95$.

It is established that in the analyzed conditions water is quantitatively extracted by methanol from alumina in 10–15 min. It is shown that there is no need to separate methanol extract from Al_2O_3 powder probe before the titration. We should note that suspensions are titrated with K.Fisher reagent comparatively seldom. The use of methylene-blue background dye provides a more clear color change in the equivalence point. Earlier E.Fisher suggested to use methylene-blue solution in ethanol or pyridine [3] for such titration, but this was not widely applied, in particular, due to ethanol hygroscopicity and the strong smell of pyridine. The change of these dissolvents to methanol makes the analysis more convenient. At evaluation 1.9 mass % water in α-Al_2O_3 with and without background dye relative standard deviation of the result was respectively 0.006 and 0.011, i.e. methylene-blue introduction caused almost two times decrease of analysis result random error.

Validity check by variation weighed portion (Table 1) showed no systematic errors in the results of water content evaluation in Al_2O_3 by the proposed methodic.

The limit of the developed methodic determination was considered the content of a defined component, for which relative standard deviation of a single result is 0.3. Concentration dependence of S_r is shown in Table 2. This dependence could be approximated by equation of a straight line $S_r = a + b(1/C)$, shown in the Figure. The results of straight line parameters by least-squares method: $a = 0.018 \pm 0.003$, $b = 0.0263 \pm 0.0007$.

The evaluation of determination limit (lower bound of the defined content) for the

Table 2. The dependence of S_r (from n parallel lines) on water content in Al_2O_3 ($\overline{C}$, mass %)

$\overline{C}$	n	S_r
3.42	3	0.022
2.15	11	0.025
1.63	3	0.040
0.64	3	0.063
0.10	4	0.280

proposed methodic, found from the mentioned equation at $S_r = 0.3$, appeared to be $9 \cdot 10^{-2}$ mass % H_2O.

Thermogravimetric study of α-alumina showed that weight losses at samples heating essentially exceed water contents found by K.Fisher method. For example, in one of the samples weight loss was 3.4±0.4 mass %, and water content was 2.15±0.04 mass %. It was supposed that at heating to 220°C Al_2O_3 evolves not only vapors but other gaseous products. The weight of the samples cooled to room temperature in the air increases almost to the initial one, according to thermogravimetric data. This testifies that alumina quickly adsorbs gaseous products from the atmosphere, which, in its turn, is caused by α-alumina high sorptive power which seems to be preserved at high temperatures.

The results of mass spectrometer analysis confirmed the assumptions. At temperature increase, we observed constant gas evolving from Al_2O_3 sample in the vacuum, the most intense — in temperature range from 25 to 200°C. Mass spectrometer analysis of gas atmosphere, formed at alumina heating up to 700°C showed that it contains not only water, but the follow ing compounds (±0.02 mass %): CO_2 — 0.93, CO — 0.32, O_2 — 0.03. Total content of the mentioned gaseous products and water, found by K.Fisher method, was 3.43 mass %, which is in good agreement with the weight loss, determined at thermogravimetric study as 3.4 mass %. One may explain the presence

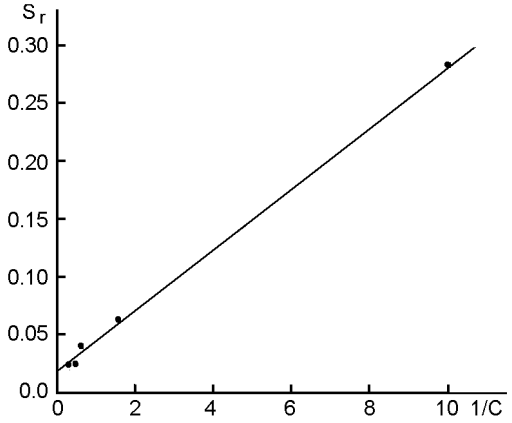

Fig. Dependence of S_r on $1/C$ (see Table 2 for initial data).

of CO_2 and CO in alumina by the fact that carbon dioxide is used in the technology of α-Al_2O_3 obtaining, and CO is generated by CO_2 thermal dissociation.

It is obvious that one can not correctly determine water content in alumina by the commonly used method of samples drying to constant mass. Constitutive amounts of water and some gases in α-alumina used for single crystals growing are, obviously, the main reason of blowhole-like defects appearing in those single crystals [1]. We can suppose that material degassing by heating it in vacuum can allow a more effective elimination of such defects in the crystals, than the widely used thermal treatment of the material at atmospheric pressure.

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Дослідження газотвірних домішок в α-оксиді алюмінію, застосовуваному для вирощування монокристалів

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Установлено оптимальні умови визначення вмісту води в α-Al_2O_3, зокрема, перемішування зразка з метанолом із подальшим титруванням одержаної суспензії реактивом К.Фішера у присутності фонового барвника — метиленової синьої. Відсутність значущих систематичних похибок доведено за допомогою методу варіювання наважок. Межа визначення розробленої методики, що відповідає відносному стандартному відхиленню одиничного результату 0,3, дорівнює $9 \cdot 10^{-2}$ мас.%. За даними термогравіметрії та мас-спектрометрії встановлено, що, крім води, α-Al_2O_3 містить значні кількості CO і CO_2, що, очевидно, є причиною появи в цих монокристалах дефектів у вигляді газових бульбашок. Висловлено припущення, що дегазація сировини нагріванням у вакуумі дозволить більш ефективно запобігати утворенню в кристалах вказаних дефектів, ніж термообробка сировини за атмосферного тиску, яку часто використовують.