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EVALUATION OF THE SURFACE ENERGY OF DISPERSED ALUMINIUM OXIDE USING OWENS-WENDT THEORY

Знання значення поверхневої енергії порошкових матеріалів дозволяє спрогнозувати взаємодію твердої фази з рідинами, формування стійких дисперсій, довговічних і стійких до агресивних факторів композитів. Розглядається застосування моделі Оуенса-Вендта для визначення зміни поверхневої енергії оксиду алюмінію, модифікованого різними гідрофобізаторами. Також, для визначення кута змочування поверхні модифікованого матеріалу використовується метод Уошбурна, який полягає у визначенні швидкості капілярного підняття випробуваної рідини. Даний метод був обраний через низькі вимоги в точності вимірювального обладнання і в той же час проявляє високу ступінь точності результатів.

Об'єктом дослідження є методика визначення поверхневої енергії порошкових матеріалів, на прикладі оксиду алюмінію модифікованого поліметилгідрідсілоксаном. Модифікація поверхні порошку оксиду алюмінію проводилася в суспензії ксилолу.

В роботі визначення поверхневої енергії було проведено відповідно до теорії Оуенса-Вендта графічним методом відповідно до отриманих значень кута змочування матеріалу за методом Уошбурна. Було встановлено форму частинок оксиду алюмінію та їх середній розмір, а також розрахована питома поверхня матеріалу. Знайдено модифікатор – поліметилгідрідсілоксан, з використанням якого вдалося отримати стабільний супергідрофобний стан, і оптимальну концентрацію шляхом визначення кутів змочування тестовими рідинами порошкового матеріалу за методикою, запропонованою Уошбурном.

Для збільшення точності визначення поверхневої енергії матеріалу за методом Уошбурна була застосована суміш води з етанолом, а також розраховані компоненти поверхневого натягу. Показано, що значення кута змочування поверхні дисперсного матеріалу, отримані з використанням в якості тестової рідини суміш, можуть бути використані для розрахунку значень компонентів поверхневої енергії оксиду алюмінію. При цьому спостерігається відсутність похибки у вигляді стану Кассі, яке спостерігається для гідрофобних дисперсних матеріалів при використанні води в якості тестової рідини.

Ключові слова: *оксид алюмінію, модель Оуенса-Вендта, метод Уошбурна, поверхнева енергія, поверхневий натяг.*

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1. Introduction

Knowledge of the surface energy of powder materials allows one to predict the interaction of the solid phase with liquids, the formation of stable dispersions, durable and resistant to aggressive factors of composites [1]. Existing models of surface energy – from Zisman (one-component) to Van Oss (three-component), are suitable only for certain types of materials [2, 3]. For example, to characterize the surface of oxides, a model involving an acid-base interaction is used, and for polar polymers, the Owens-Wendt model. The paper considers the application of the latter model to determine changes in the surface energy of aluminium oxide modified by various water repellents. Also, the Washburn method [4, 5] is used to determine the contact angle of the surface of the modified material [4, 5], which consists in determining the rate of capillary rise of the test fluid. Of the two methods for implementing this method – determining the mass gain rate and the layer climb speed – the second one is chosen, since it does not require such accurate measuring equipment, but it exhibits a rather high degree of accuracy of the results [6–8]. Thus, *the object of research* is a method for determining the surface energy of powder materials, for example, aluminium oxide modified with polymethylhydrosiloxane. *The aim of research* is to describe a simple algorithm for determining the surface energy of powder materials.

2. Methods of research

The studies were carried out using white aluminium oxide 25A/M2 (GOST 3647-71) (Boksitogorsk plant of the «Glinozem» production association, Russia), which is aluminium oxide with a density of 3.93–4.1 g/cm^3 and an average particle size of 2 μm.

The following modifiers were used: a mixture of cyclopentasiloxane and dimethicone BC 2335 (KCC Basildon, Great Britain), methyltriethoxysilane Dynasylan MTES (Evonic, Germany), aminopropyltriethoxysilane Dynasylan AMEO (Evonic, Germany) and polymethylhydrosiloxane Xiameter MHX 1107 (Dow Corning, USA). Xylene was used as a solvent for silanes.

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To modify the surface of the powder into a suspension of aluminium oxide in xylene, the required amount of modifier was dosed: 0.05; 0.07; 0.1; 0.3 and 0.5 mass %. The prepared samples were dried on the surface of the watch glass for 24 hours without heating.

To determine the contact angle of prepared samples with test liquids, the Washburn thin-walled capillary impregnation technique was used. Samples were prepared in the form of a 5 % suspension in isopropyl alcohol and applied to the glass surface with dimensions of 4×8 mm. After drying the suspensions, markings were applied on the surface of the layer (three consecutive marks with a distance of 1 mm). Samples were conditioned in vapors of the test fluid and then measured the passage time between the marks of the wetting front during immersion.

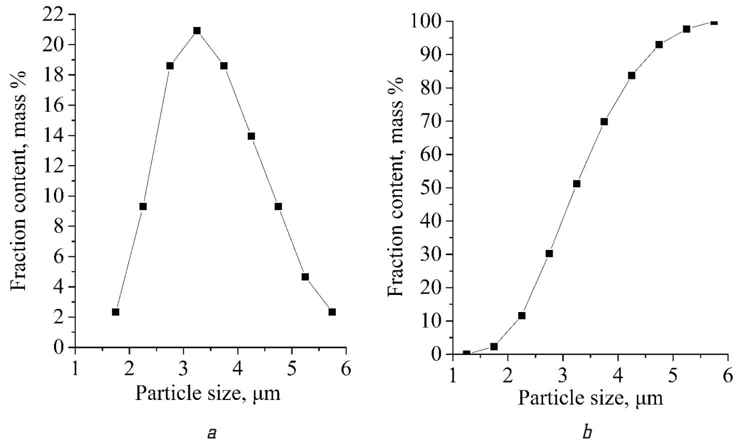

Fig. 2. Particle size distribution: *a* – differential curve; *b* – integral curve

The wetting time was recorded using a video camera with an accuracy of 0.1 s. The number of time measurements for each solvent was 5 times, and the average measurement error in the entire array of solvents was 6.9 %. For calculations, the modified Washburn equation (1) was used, assuming that the most non-polar liquid – hexane completely wets the surface, i. e. the cosine of the contact angle approaches unity.

$$\cos\theta = \frac{\mu_t \cdot \sigma_0}{\mu_0 \cdot \sigma_t} \cdot \frac{t_0}{t_t}, \qquad (1)$$

where μ – the dynamic viscosity of the liquid; σ – its surface tension; t – the travel time of the front between the marks; index 0 corresponds to hexane, index t corresponds to test fluid.

The surface energy was determined in accordance with the Owens-Wendt theory by the graphical method in accordance with the values obtained by the Washburn method for the contact angle of the material with test liquids [9, 10].

3. Research results and discussion

It is established that the particles of aluminium oxide have an irregular, fragmentation shape (Fig. 1). The closest geometric figure is a prism. The average particle size is 3.3 μm, while the distribution of their sizes (Fig. 2, *a*, *b*) is monomodal and quite narrow – with a minimum particle size of 1.6 μm and a maximum of 6.3 μm. The calculated specific surface area of the material, provided there is no capillary porosity of the particles, is 2800 cm^2/g.

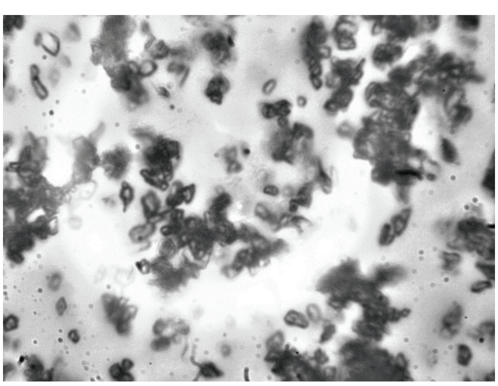

Fig. 1. Optical microscopy of aluminium oxide particles

Of all the surface modifiers tested, provided that they were dried under atmospheric conditions, only Xiameter MHX 1107 allows to obtain a stable superhydrophobic state, which is characterized by the rolling of drops of distilled water from the surface of the powder sample at the end of processing. This state is observed for modifier concentrations equal to and above 0.1 mass % by weight of aluminium oxide and, probably, is a consequence of a decrease in the polar component of surface energy. This assumption is verified by determining the contact angles of the powder material with test liquids according to the method proposed by Washburn, and hexane is used as test liquid. ethanol and distilled water, as well as a mixture of the last two solvents.

Graph in Fig. 3 is a combination of the measurement results by the Washburn method (up to a modifier concentration of 0.1 mass %) with the results of measuring the contact angle by the sitting drop method (0.1 mass % and higher).

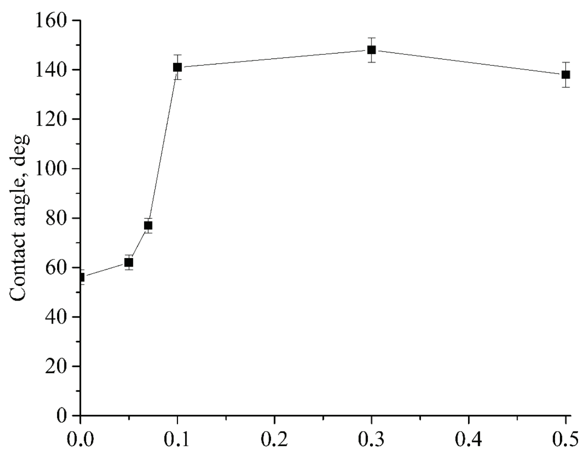

Fig. 3. Change the contact angle of the aluminium oxide surface

Noteworthy is the sharp jump in the contact angle in the concentration range of polymethylhydrosiloxane from 0.07 to 0.1 mass %. However, it is likely that when using water as a test fluid in the sitting drop method, a Cassie state is achieved. This introduces a certain error in the measurements and does not allow to accurately determine the surface energy of the material.

To solve this problem in the Washburn method, water as a test fluid is replaced with its mixture with ethanol. The components of the surface tension of the mixture were calculated in accordance with the procedure [11].

Fig. 4 shows that the change in the dispersion and polar components of the energy of the surface of aluminium oxide with increasing concentration of the modifier most pronounced occurs in the range from 0.05 to 0.1 mass %. A significant decrease in the polar component is associated with the screening of the active functional groups of the oxide surface by a nonpolar modifier [12].

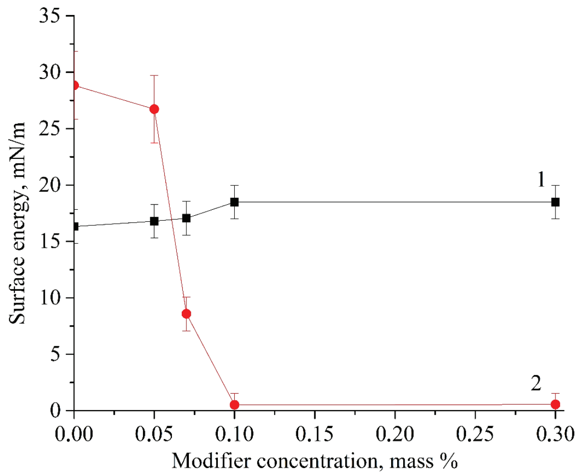

Fig. 4. The dependence of the Al_2O_3 surface energy components depending on the concentration of polymethylhydrosiloxane: 1 – dispersed; 2 – polar

It is worth noting that for cases of hydrophobic material it is possible to choose a mixture of ethanol and water, the surface contact angle of which will be 90 degrees. In this case, the ordinate of the solvent point in the Owens-Wendt graphical method takes the minimum value:

$$y = \frac{\sigma_L}{2\sqrt{\sigma_L^D}}, \quad (2)$$

where σ_L – the surface tension of the test fluid, and σ_L^D – the dispersion component of its surface tension.

4. Conclusions

It is established that the white aluminium oxide used in the work has a monomodal distribution of particles, the average size of which is 3.3 μm. The most effective modifier for the surface of this material is Xiameter MHX 1107 polymethylhydrosiloxane.

It is shown that the contact angle of the surface of the dispersed material obtained by the Washburn method using a mixed solvent (water-ethanol) as a test fluid can be used to calculate the values of the surface energy components of aluminium oxide. There is no error in the form of the Cassie state, which is observed for hydrophobic dispersed materials when using water as a test fluid.

The value of the effective concentration of the modifier, which is 0.1 mass % by weight of the dispersed material. Moreover, a sharp drop in the share of the polar component of its surface energy occurs, starting from 0.05 mass % modifier.

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