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Wettability of sapphire

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Presented are the study results of wetting of main crystallographic surfaces of sapphire with water and glycerin by measuring the wetting angle of a rest drop. It is shown that, depending on the surface function of a sapphire, both maximum and minimum wetting can be attained by varying the crystallographic orientation.

Представлены результаты исследования смачивания основных кристаллографических поверхностей сапфира водой и глицерином. Использован метод измерения краевого угла покоящейся капли. Показано, что в зависимости от функции поверхности сапфира, можно достигнуть как максимального, так и минимального смачивания путем варьирования кристаллографической ориентации.

The effectivity of sapphire use in chemical engineering and in medical implants is defined, among other factors, by the wetting of its surface with liquid substances in contact. The wettability is among the "bioactivity" factors of the implant surface. Depending on the surface destination, both the maximum and minimum wetting may be required. At the same time, there are substantially no literature data on the sapphire wetting. In [1] dealing with the contact wetting angle, the surface free energy of sapphire has been determined to be of 52.95 erg/cm^2, but the corresponding crystallographic plane has been identified. In the mineralogical literature, the wettability characteristics of 92° to 80° are indicated most often, these data being not associated with crystallographic characteristics, too. That is why the angular range is so broad. Sapphire is anisotropic, thus, the surface free energy values differ considerably for various crystallographic planes. This work deals with wettability determination for main crystallographic planes of pure and doped sapphire.

The wettability is characterized quantitatively by the wetting angle Q^0 formed at a solid surface along the phase interface. The value, according to Foxe equation, is related to the material surface energy and depends on the surface free energy (SFE) values of three phase interfaces being in contact at the wetting line (s-l, s-g, l-g) as follows:

$$\cos Q = \frac{\sigma_{s-g} - \sigma_{s-l}}{\sigma_{l-g}}.$$

It is the number of free bonds per unit surface area (Table) [2] that can be considered as an approximated measure of that energy.

In real crystals the SFE depends on the number, type, and distribution of structure defects. To unify these parameters, the crystals were grown at the speed of 10±2 mm/h and annealed in vacuum at 1950±5°C. Then 10 mm thick disks of 18 mm in diameter were cut out of the crystals, the orientation error was less than 1°. The sample surfaces polished to $R_z = 0.05$ μm were wiped with cheap cotton wetted with

Table. Wear rate of leucosapphire (mm/h)

Characteristics of the sample plane				Abrasive type					
				Free abrasive, boron carbine N4				Fixed abrasive, ACM80/63	
Plane	d, Å	n	E_f, J/m^2	Load ×10 , kg/mm^2					
				3	5	7	11	2.2	5
(0001)	2.165	6.6	5.44	1.97	2.52	3.48	3.84	2.12	7.12
$\{10\bar{1}2\}$	3.479	3.5	~1.3	2.49	3.38	4.22	3.76	6.23	17.8
$\{11\bar{2}0\}$	2.379	4.8	1.27	3.45	4.83	6.48	7.83	2.31	8.29
$\{10\bar{1}0\}$	1.374	–	1.09	3.26	4.97	7.48	8.11	3.59	11.8

d– interplane spacing; n– number of free bonds; E_f–the surface formation energy [3].

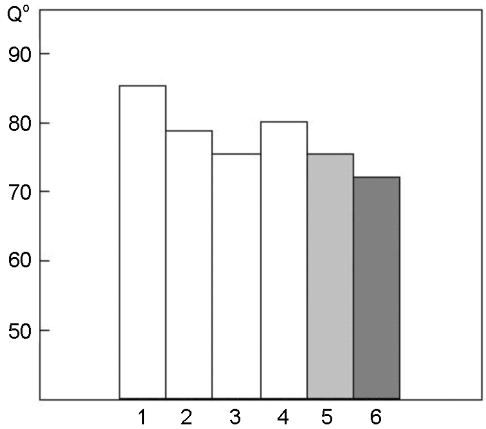

Fig. 1. Wetting angle of sapphire planes with water: 1 — (0001), 2 — $\{10\bar{1}0\}$, 3 — $\{11\bar{2}0\}$, 4 — $\{10\bar{1}2\}$, 5 — $\{10\bar{2}0\}$ (0.05 Ti), 6 — (0001) (0.1 Cr).

alcohol and then with water wetted cloth and dried in air. Measuring rest drop wetting angle Q^0 using optical microscopy [4], the wetting was studied for pure sapphire at crystallographic planes (0001); $\{10\bar{1}0\}$; $\{11\bar{2}0\}$; $\{10\bar{1}2\}$ and for crystals doped with 0.1 % Cr at (0001) plane and with 0.05 % Ti at $(11\bar{2}0)$ one. The surface was wetted with distilled water, glycerin, and isotonic solution (0.9 % NaCl) in air at 25°C. The wetting angle measurement error was 0.5 to 1.3 %.

The wetting angles for the main crystallographic planes of sapphire are within 68 to 85° range both in polar liquid (distilled water) and non-polar one (glycerin) (Figs. 1, 2). The non-polar glycerin wets the surfaces of all samples studied better than water. The crystallographic orientation and dopants effect weaker the Q^0 value, although the general variation character remains unchanged. The crystal doping is a factor of importance enhancing the wettability. Doping with Cr (C = 0.1 %) causes $Q^0_{(0001)}$ decrease by 12° and 8° for water and glycerin, respectively. The same effect is revealed at Ti doping (C ~ 0.05 %), the $Q^0_{(1120)}$ decrease amounting 3°. In isotonic NaCl solution (C = 0.9 %), the crystal composition and crystallographic parameters are observed to influence the wettability, too, but the variation trend does not correlate with the data on other liquids in all the cases. This can be explained by difference in effects of the solution ionic components (Na^+ and Cl^-) on the physicochemical sorption processes at the planes studied. The values of surface energy for the sapphire crystallographic planes estimated from the wetting angles are in correlation with the results of wear resistance tests carried out before (Table). The maximum wear rate with free abrasives is seen to correspond to minimum Q^0 values (maximum energy) in water for $\{10\bar{1}0\}$ and $\{11\bar{2}0\}$ (see Fig. 1). This evidences that water is involved actively in the wearing process as a surface-active substrate. The maximum biological inertness of a sample corresponds to minimum surface energy and, respectively, to

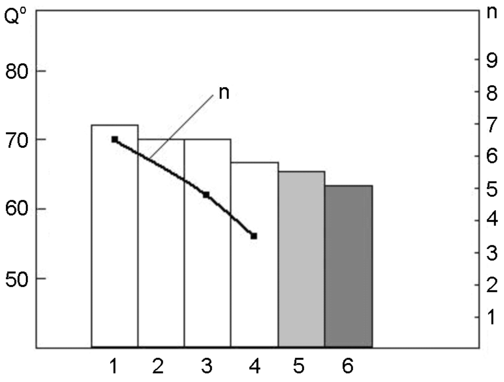

Fig. 2. Wetting angle of sapphire planes with glycerin: 1 — (0001), 2 — $\{10\bar{1}0\}$, 3 — $\{11\bar{2}0\}$, 4 — $\{10\bar{1}2\}$, 5 — $\{10\bar{2}0\}$ (0.05 Ti), 6 — (0001) (0.1 Cr).

the maximum possible wetting angle [5]. These data are in correlation also with corrosion resistance of various crystallographic planes of sapphire [6].

The physicochemical processes in the treatment area in the presence of water can be described briefly as follows. At the crystal/liquid interface, considerable adhesion forces occur between the liquid boundary layer molecules and the crystal surface. These forces hinder the sliding at the interface. The wetting phenomenon is explained usually by such an interaction of force fields. The surfaces in friction are separated as a rule by a thin lubricant layer that is connected so strongly thereto that their direct contact is excluded, and the relative displacement occurs along the intermediate liquid layer. The surface activity of a liquid depends on its molecular structure, the activity being the stronger, the higher is the molecular polarity. As the liquid molecules adsorbed at the crystal surface are mobile, the molecular interaction is propagated into the crystal near-surface layer along the microcracks. The wedging effect of the liquid molecules (the Rebinder effect) develops the microcracks towards macro-cracks and thus causes the shearing of particles from the crystal surface, so the dispersion process is facilitated [7]. Since water wets the $\{10\bar{1}0\}$ and $\{11\bar{2}0\}$ planes better during the grinding, it is just these planes where the maximum wear rate is observed.

Thus, the dependence of sapphire wetting with water and glycerin on the crystallographic orientation has been studied. The wetting angle for both liquids is maximum at the (0001) plane. The minimum wetting angle values are observed at $\{10\bar{1}0\}$ and $\{11\bar{2}0\}$ for water and at $\{10\bar{1}2\}$ for glycerin. A correlation has been found between the water wettability of the main crystallographic planes of sapphire and the wear rate of those planes under grinding with free abrasive using water as the suspension medium.

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Змочуваність сапфіру

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Представлено результати вивчення змочування основних кристалографічних поверхонь сапфіру водою та гліцерином. Використано метод вимірювання крайового кута каплі, що перебуває у стані спокою. Показано, що в залежності від функції поверхні сапфіру, варіюючи кристалографічною орієнтацією, можливе отримання як максимального, так і мінімального змочування.