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Potentialities for sapphire strength enhancement

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The study results are presented concerning the influence of technological factors, such as annealing atmosphere and mechanical treatment, on the sapphire strength. The ultimate strength under four-point flexure has been determined according to European standard EN 843-1:1995 using the four-point-1/4-point flexure scheme. The high-temperature annealing in various atmospheres that defines the stoichiometric composition has been shown to influence the mechanical characteristics of sapphire.

Представлены результаты исследования влияния технологических факторов, таких как, среды отжига и механической обработки, на прочность сапфира. Предел прочности при четырехточечном изгибе определялся согласно Европейскому стандарту EN 843-1:1995 с применением схемы Four-point-1/4-point flexure. Показано, что высокотемпературный отжиг в различных средах, определяя стехиометрический состав, существенно влияет на механические характеристики сапфира.

The sapphire use in friction joints of high-precision instruments, nozzles, medical implants, etc., as well the intensification of machining regimes, makes it necessary to study more deeply the effect of technological factors on the sapphire strength.

The data on annealing effect in variation of strength characteristics are contradictory [1]. In [2–4], the flexure strength limit of sapphire was studied as a function of temperature. The structure (blocking, dislocation density) and geometric parameter of the samples, the crystal pre-history, and measurement procedures varied considerably, that is why the absolute results showed significant scattering (Fig. 1). Comparison of the data obtained by Gentilman for 0° and 60° orientation sapphire evidences that the strength drops of the 0° samples at 500°C due to basal sliding along the cleavage planes and becomes lower than that of the 60° samples. At room temperature, the strength of 0° samples exceeds considerably that of the 60° ones. In [5], the sapphire strength was studied also at various temperatures and depending on its crystallographic orientation. However, the structure parameters were not controlled; besides, the procedure of ultimate strength determination under four-point flexure differs considerably from the European and American standards now in action, therefore, the strength values obtained are difficult to compare with the data from other sources. Moreover, the influence of the impurity composition on the strength characteristics has not been studied in [2–5], although some impurities undoubtedly reinforce the crystal due to deceleration of the plastic straining under loading. The cited works do not consider the effect of annealing that may result both in strengthening and embrittlement, depending on the redox potential of the annealing atmosphere and the impurity composition of the crystal. The blocking influences the strength substantially, too. Thermally activated processes may cause the block formation and decoration during the annealing and reduce the strength (Fig. 2).

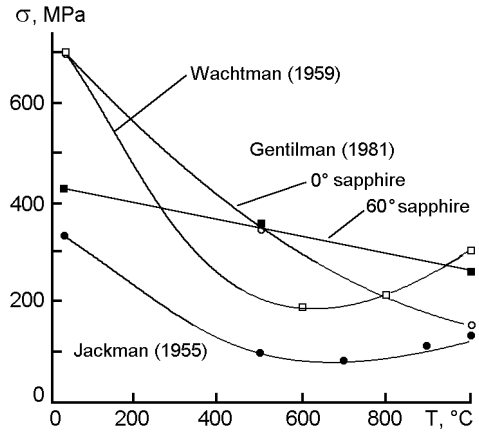

Fig. 1. Flexural strength of sapphire. Wachtman: 4-point flexure, polished bar orientation C; Jackman: 4-point flexure, arbitrarily oriented 2×2×58 mm^3 bar; Gentilman: biaxial bending of a 51×2.5 mm^2 disc at the normal C and 60° to C axis.

The ultimate strength under four-point flexure has been determined according to European standard EN 843-1:1995 using the four-point-1/4-point flexure scheme [6]. To that end, the crystals were grown using the HDC and Kyropoulos technique from the raw blend consisting of the Verneuil sapphire breakage with fixed impurity composition (see Table). The block-free samples were made of the crystals shaped as rectangular bars of 4×3×45 mm^3 (sample width × thickness × length). In sapphire, it is just the (0001) plane that is the easy sliding one. That is why the bar orientation was selected to avoid the sliding planes positioning directly on the fracture line (Fig. 3). The ground and polished bars were examined. The ground samples were finished by free abrasive (boron carbide No.5) up to R_a = 1.2 μm roughness using a 3ShP-350M machine while the polished ones, by ASM 28/20 diamond powder up to R_a = 0.4 μm roughness using a 4PD-200 machine. The dislocation density in the samples was examined by selective etching on the (0001) plane, the values obtained were within the range of $1 \cdot 10^3$ to $4 \cdot 10^3$ cm^{-2}. The blocked samples were discarded.

The samples were annealed successively in vacuum (a SShVL furnace, temperature 1870°C, residual pressure $2.6 \cdot 10^{-2}$ Pa, duration 4 h), then in hydrogen (OVP furnace, 1750°C, 10^5 Pa, 10 h). The tests were carried out using a 2054P5 tearing machine at straining rate about 0.5 mm/min.

At the four-point flexure tests, the loading assembly for the force transmission onto the sample comprises two parallel cylindrical rollers spaced by 20 mm. The time from the sample loading onset to its splitting into parts amounts from 3 to 30 s. When testing, the force applied to the sample at its breaking was determined. The ultimate strength σ (MPa) of a sample was determined as $\sigma_{flex} = 3P_m a \cdot b^{-1} \cdot h^{-2}$, where P_m is the force value at the sample breaking, N; a, the sample console length ($a = L/4$), mm; b, the sample width, mm; h,

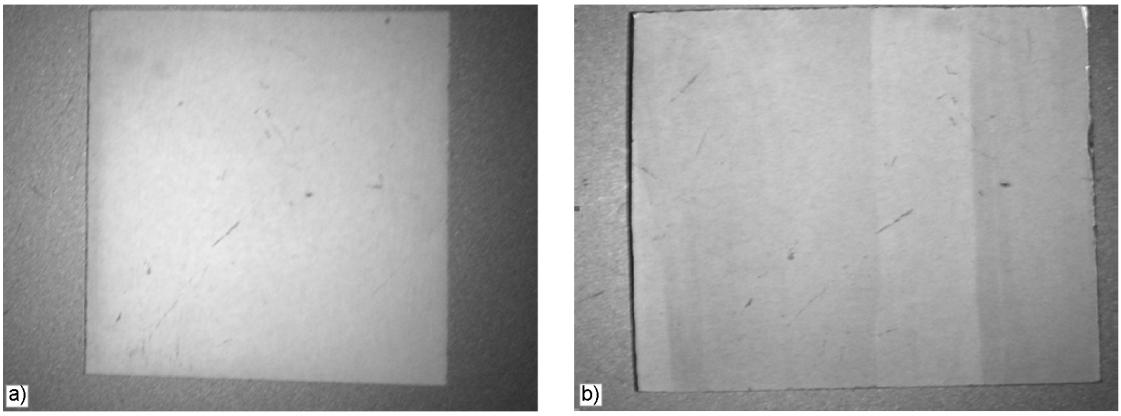

Fig. 2. Block formation under annealing: block-free crystal (a); blocks formed during the high-temperature annealing (b).

Table. Impurity content in the studied crystals

Element	Fe	Si	Mg	V	Cr	Ti	Mo
Mass.%	$2 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	$2 \cdot 10^{-3}$	$<1 \cdot 10^{-4}$	$<5 \cdot 10^{-4}$	$7 \cdot 10^{-3}$	$<1 \cdot 10^{-4}$

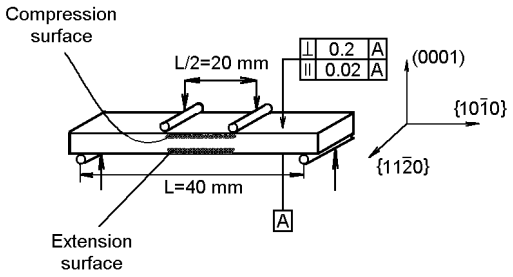

Fig. 3. 4-Point flexure testing scheme for a sapphire bar.

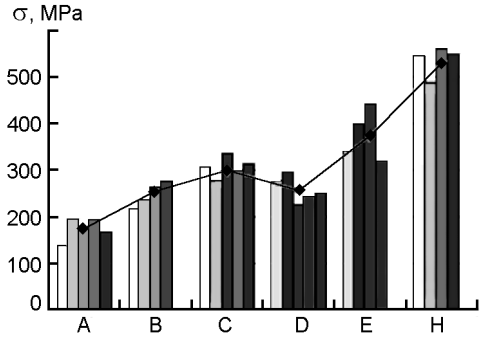

Fig. 4. Ultimate strength σ of sapphire samples under 4-point flexure as depending on the surface state and annealing atmosphere. A, the initial state; B, ground samples annealed in vacuum; C, ground samples annealed successively in vacuum and in hydrogen; D, samples ground additionally; E, polished samples annealed in vacuum; H, polished samples annealed successively in vacuum and in hydrogen.

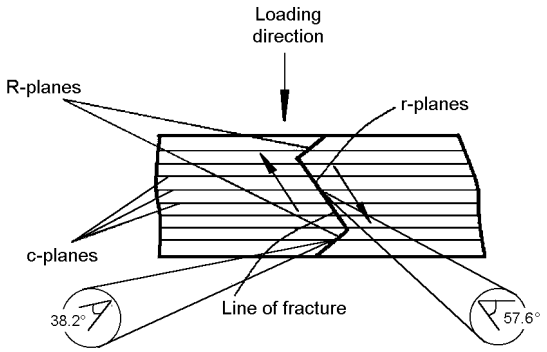

Fig. 5. Breaking line at separation of a sapphire bar into parts.

the sample thickness in the direction parallel to that of the force application, mm.

At the first work stage, all the samples were annealed in vacuum to relax the internal stresses and recrystallize the defect near-surface layer. The strength of ground samples was increased by 25–42 % as compared to the initial state (that is, after growing, cutting, and surface grinding). The maximum strength increase was attained by successive anneals in vacuum and hydrogen. The sapphire strength was enhanced by 60–70 % (Fig. 4).

The surface state influences the strength considerably. The ultimate strength of polished samples after the hydrogen annealing exceeds by 62–78% that of corresponding ground ones and by 41–64 % that of the initial samples (Fig. 4). This is due to minimization of defect surface layer during the sample polishing and to corresponding reduction in the size and amount of microcracks that are the sources of crack formation and subsequent breaking during the loading. The depth of defect surface layer is about 40 to 45 μm for ground samples and 1 to 5 μm for polished ones, as determined by layer-to-layer etching up to $\rho = \text{const}$. The strength increase can be associated with the dislocation density reduction due to annealing [1] as well as an increased dislocation mobility at hydrogen annealing [7]. Some samples annealed successively in vacuum and in hydrogen were machined (ground) additionally, thus causing the strength reduction by 15–20 % from the maximum value.

No strength differences have been revealed between the samples made from crystals grown by HDC and Kyropoulos technique, perhaps due to similar structure characteristics of the crystals.

When considering the fracture lines, the samples have been found to cleave mainly along {10$\bar{1}$1} and {10$\bar{1}$2} planes (Fig. 5). At the cleavage along the {10$\bar{1}$1} planes, the cracks are propagated along the twinning planes that are observed predominantly at highest straining rates corresponding to the flexure straining conditions of sapphire sample.

Thus, the high-temperature annealing atmosphere that defines the stoichiometric composition influences considerably the mechanical characteristics of sapphire. The vacuum annealing enhances the strength by 25–42 % as compared to the initial state. The flexural strength of sapphire after successive anneals in vacuum and hydrogen increases by 60–70 %. The ultimate strength of polished samples annealed in hydrogen exceeds by 62 to 78 % that of ground ones due to minimization of defect surface layer during the sample polishing and to corresponding reduction in the size and amount of microcracks. To enhance the strength of sapphire articles, the mechanical treatment should be followed by high-temperature annealing.

References

1. E.R.Dobrovinskaya, L.A.Litvinov, V.V.Pishchik, Encyclopaedia of Sapphire, Inst. for Single Crystals Publ., Kharkiv (2004) [in Russian].
2. J.B.Wachtman, Jr. and L.H.Maxwell, *J.Am. Ceram. Soc.*, **42**, 432 (1959).
3. E.A.Jackman, J.P.Roberts, *Phil.Mag.*, **46**, 809 (1955).
4. R.L.Gentilman, E.A.Maguire, H.S.Starrett et al., *J.Am.Ceram.*, **64**, 116 (1981).
5. D.C.Harris, in: Proc. SPIE Conf. Window and Dome Technologies and Materials, VI, **3705**, 2 (1999).
6. Procedure of Flexure Ultimate Strength Determination: DSTU 3716-98, Derzhstandart Ukrainy, Kyiv (1998) [in Ukrainian].
7. J.Kvapil, *Kristall und Techik.*, **6**, k1 (1971).

Можливості підвищення міцності сапфіру

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Представлено результати вивчення впливу таких технологічних факторів як середовище відпалу та механічна обробка на міцність сапфіру. Визначення межі міцності при чотириточковому згинанні проводилося відповідно до європейського стандарту EN 843-1:1995 за схемою Four-point-1/4-point flexure. Показано, що високотемпературний відпал у різних середовищах, визначаючи стехіометричний склад, впливає на механічні характеристики сапфіру.