

Phase transformations of α - Al_2O_3 during annealing in a reducing atmosphere

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Study results of corundum structure transformations due to annealing of α - Al_2O_3 in Ar atmosphere containing a reducing component ($\text{CO} + \text{H}_2$) at 1700–1900°C are presented. It has been found that a polycrystalline layer containing new phases is formed at the single crystal surface during the annealing under a high evaporation rate. One of those phases belongs to the Fd3M cubic syngony (spinel) while another one has hexagonal structure (P63/mmc space group). A qualitative model has been proposed for the observed α - $\text{Al}_2\text{O}_3 \rightarrow \text{AlAl}_2\text{O}_4$ (spinel) transformation involving the hexagonal phase.

Представлены результаты исследований трансформации структуры корунда в результате отжига α - Al_2O_3 в атмосфере Ar с восстановительной компонентой ($\text{CO} + \text{H}_2$) при температуре 1700–1900°C. Установлено, что на поверхности монокристаллических образцов на фоне высокой скорости испарения при отжиге образуется поликристаллический слой, содержащий новые фазы. Одна из обнаруженных фаз относится к кубической сингонии Fd3M (шпинель), другая — имеет гексагональную структуру (пространственная группа P63/mmc). Предложена качественная модель наблюдаемого превращения α - $\text{Al}_2\text{O}_3 \rightarrow \text{AlAl}_2\text{O}_4$ (шпинель) с участием гексагональной фазы.

The interest in the problem of high-temperature corundum-to-spinel (AlAl_2O_4) phase transformations at a high reduction rate of Al_2O_3 is associated with the necessity to explain the nature of light scattering centers being formed in sapphire crystals grown in reductive atmospheres [1]. Later, we have found that the near-surface layer of Al_2O_3 can be transformed into a spinel type f.c.c. structure by annealing in reducing conditions [2]. In this work, the phenomenon is studied in more detail.

Studied were ground and polished plane-parallel sapphire samples with surface crystallographic orientation (0001) and (10T2), (10T0) as well as finely dispersed Al_2O_3 powders. The annealing was carried out in a furnace with carbon-graphite heat screens [3] at 1700–1900°C. After the preliminary vacuum treatment and evacuation down to about 0.1 Torr residual pressure, the furnace chamber was filled with Ar or an Ar mixture with reducing additives (CO , H_2 ,

$\text{CO} + \text{H}_2$) up to 800 Torr pressure. The reducing component ($\text{CO} + \text{H}_2$) concentration in the gas medium was controlled using a "Gazokhrom 63101" gas analyzer. The annealing lasted from 2 to 10 h. The sample temperature was monitored by a W + 5 % Re–W + 20 % Re thermocouple calibrated preliminarily by reference points. The X-ray phase analysis (XPA) was carried out using a DRON-1.5 diffractometer in Cu $K_{\alpha 1,2}$ radiation with pyrolytic graphite (002) monochromator according to the θ – 2θ scheme. The thickness of polycrystalline zone formed on the sapphire substrate was determined both under approximation of a homogeneous screen weakening the single crystal reflections [4] and from the intensity of intrinsic interference lines in symmetric Bragg geometry [5]. The changes in the substrate structure perfection were analyzed using the sliding angle (α) variation of the X-ray beam at the sample discrete rotation about the diffraction vector for

asymmetric Bragg case [6]. The α values at the swinging curve survey were from 1 to 8°, Cu K α_1 radiation with Ge(111) monochromator ($n, -m$) scheme was used.

The near-surface layer of the single crystal samples has been found to be transformed due to the reducing annealing into a polycrystalline one consisting of new phases. It follows from the powder diffraction pattern that one of those phases belongs to the Fd3M cubic syngony (spinel) while another one has hexagonal structure of P63/mmc space group (referred to as H-phase from here on). Similar phase transformations are observed when thin (about 0.5 mm) layers of α -Al $_2$ O $_3$ powders are annealed. No traces of carbon or aluminum oxycarbides have been found in polycrystalline layer on the crystal surface or in the powders, at least within limits of XPA sensitivity.

Fig. 1 presents the results obtained in three experimental series at various reducing potentials of the annealing atmosphere. The data shown by triangles have been obtained with the chamber filled with Ar. In this case, the reducing atmosphere in the chamber is formed spontaneously due to interaction of adsorbed oxygen and water vapor with the carbon-graphite materials. The reducing component concentration in this case does not exceed 5 %. The data noted by open circles and squares have been obtained when using the Ar + 5–10 % CO (CO + H $_2$) mixtures; those indicated by solid circles, at the use of Ar + 10 % H $_2$ mixture.

The changes in the phase composition of the sapphire substrate surface layer are seen to occur at a high evaporation rate (Fig. 1a). The transformed layer of more than 10 μ m thickness is observed at the substrate surface even if the evaporation rate exceeds 100 μ m/h. The evaporation rate increases as the annealing temperature and the atmosphere reducing potential rise [3]. In spite of a considerable data spread of the experimental data, the transformed layer thickness can be noted to tend to increase in parallel with the temperature elevation and the atmosphere reducing potential increase (Fig. 1b). In the layer, the phase composition is observed to vary from a phase mixture containing a high concentration (>90 %) of the H-phase to an essentially complete (>98 %) transition to spinel (Fig. 1c). The corundum-to-spinel conversion extent depends also on the temperature and the atmosphere reducing potential. It is seen from the Figure that the annealing in

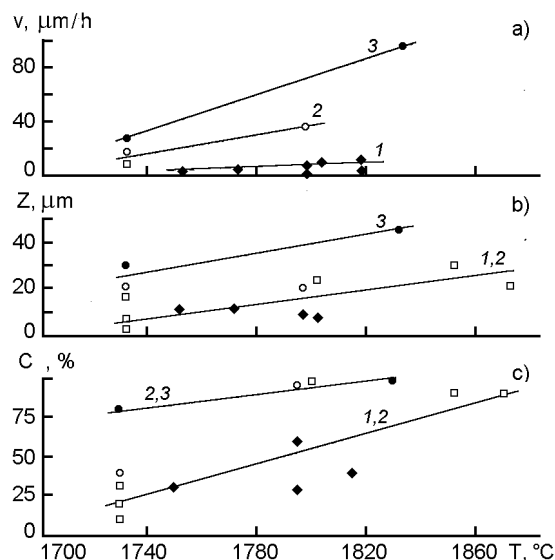


Fig. 1. Temperature dependences of evaporation rate (a), transformed layer thickness (b), and α -Al $_2$ O $_3$ to spinel conversion extent (c). Atmosphere characteristics: 1 – Ar (solid triangles); 2 – Ar + 5–10 % CO (CO + H $_2$) (light squares and circles); 3 – Ar + 10 % H $_2$ (solid circles).

a less reducing atmosphere is accompanied by a lower conversion to spinel (a high content of H-phase being observed in the layer). As the reducing potential increases, the conversion to spinel is more complete. At the same time, the spinel concentration in the layer increases as the annealing temperature rises.

The lattice periods in both phases vary considerably. The spinel lattice period (a_{sp}) values measured in various experiments are within the 7.933 to 7.948 Å range and increase as the spinel concentration in the layer rises up to 80–90 %, this trend being more pronounced in powders. At higher spinel concentrations, the (a_{sp}) values diminish. As the spinel content in the layer exceeds 98 % (at the limiting measurement sensitivity), the (a_{sp}) values do not exceed 7.9332–7.9338 Å. The lattice parameter variations are observed for the H-phase, too ($a = 3.107$ to 3.115 Å; $c = 4.984$ to 4.985 Å). Besides the isotopic component, both the H-phase and spinel are textured. At the (0001) sapphire surface, the $\langle 111 \rangle$ spinel texture and the $\langle 001 \rangle$ H-phase one are formed. The $\langle 311 \rangle$ and $\langle 111 \rangle$ spinel textures are also observed on the (10 $\bar{1}2$) and (10 $\bar{1}0$) sapphire surfaces. All the directions mentioned are normal to the surface.

More detailed studies of the textured layers have shown that the new phase are

formed inheritance the matrix crystallography. Using the oblique shooting, it has been found that the scattering angles of crystallites for both phases in the normal direction as well as in the (0001) plane can be described in terms of the rocking curve half-width β and are within 0.6 to 2.5° range. As to the <001> H-phase texture and the <111> spinel one on the (0001) sapphire surface, the C axis of the H-phase has been found to coincide with the C axis of the corundum lattice, the H-phase lattice being rotated by 30° about the C axis; in the case of spinel, the <112> direction coincides with the <100> one of the matrix. The "inheritance" link is observed even if the sapphire substrate surface is inclined by about 10° to the crystallographic plane. Both phases are stable under normal conditions. The diffraction pattern of the transformed layer remains unchanged when annealed in air at 700–800°C. The annealing in air at about 1300°C results in the complete transformation of both phases into corundum, the sample mass increases after that treatment. Assuming that the mass increase is due to oxygen absorption, the composition of the new phases can be estimated. According to such estimations, if the Al/O ratio in those compounds is the same, the composition thereof is within limits $\text{Al}_{2.86}\text{O}_4$ to $\text{Al}_{2.92}\text{O}_4$ (or $\text{Al}_2\text{O}_{2.8}$ to $\text{Al}_2\text{O}_{2.74}$).

Thus, the annealing of $\alpha\text{-Al}_2\text{O}_3$ in a reducing atmosphere has been found to result in corundum transformation into new phases within the surface layer of the initial material. As these changes occur at high evaporation rate, the condensation from gas phase cannot be the formation cause thereof. That cause consists more likely in a "catastrophic" distortion of the corundum structure stoichiometry under oxygen depletion of the layer contacting with the reducing atmosphere. This supposition is confirmed by dependence of the layer thickness (Fig. 1b) and the corundum-to-spinel conversion extent (Fig. 1c) on the reducing potential of the atmosphere (that defines the concentration of oxygen vacancies) and the temperature (defining the diffusion mobility thereof).

When considering the mechanism of the corundum \rightarrow spinel phase transition, to study the H-phase structure and its part in the observed transformation is of considerable interest. All the interference lines of that phase have been found to answer to hexagonal structure (P 63/mmc space group) with lattice periods $a = 3.107$ to 3.115 \AA and $c = 4.984$

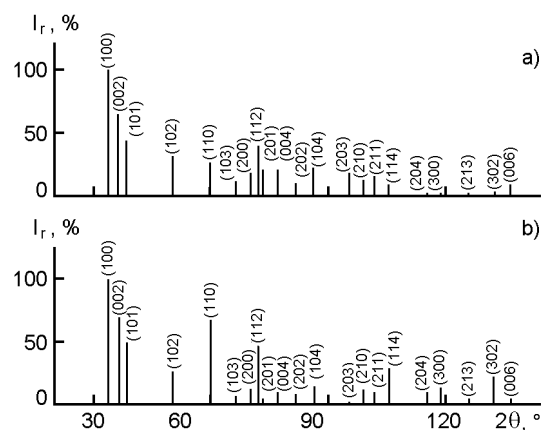


Fig. 2. Experimental (a) and calculated (b) diffraction patterns for H-phase. $\text{Cu K}\alpha_{1,2}$ radiation.

to 4.985 \AA . The H-phase cannot be identified as one of the known hexagonal Al_2O_3 phases (β , χ , ϵ). The phase analysis handbook [7 p.626], is the only source including a similar Al_2O_3 phase with similar lattice periods ($a \approx 3.10 \text{ \AA}$, $c \approx 4.99 \text{ \AA}$), but no detailed information is cited. The preliminary analysis has shown that a hypothetical structure of variable composition can be used as an approximate model for the H-phase (see Table 1). The occupancy of the 2a symmetry position equal to 0.5 corresponds to the Al_2O_3 composition while 0.333, to $\text{Al}_2\text{O}_{2.667}$ (Al_3O_4) one. The comparative characteristics of experimental and calculated diffraction pattern for the structure with $a \approx 3.107 \text{ \AA}$ and $c \approx 4.984 \text{ \AA}$ are presented in Fig. 2. The calculated and experimental data coincide qualitatively while the calculated ones for $\text{Al}_2\text{O}_{2.667}$ agree somewhat better with the experiment than those for Al_2O_3 . But there is no satisfactory quantitative agreement in both cases. In our opinion, as the texture is present in the transformed layer and the temperature factor was not taken into account in calculations, the structure model proposed can be used to describe the new phase only approximately.

The interference lines of the spinel phase answer to cubic structure (Fd3m space

Table 1. Structure data of H-phase.

Atom	Position	Coordinates			Occupancy
		x	y	z	
Al	2b	0	0	0.25	1
O	2c	0.3333	0.6667	0.25	1
O	2a	0	0	0	0.5–0.333

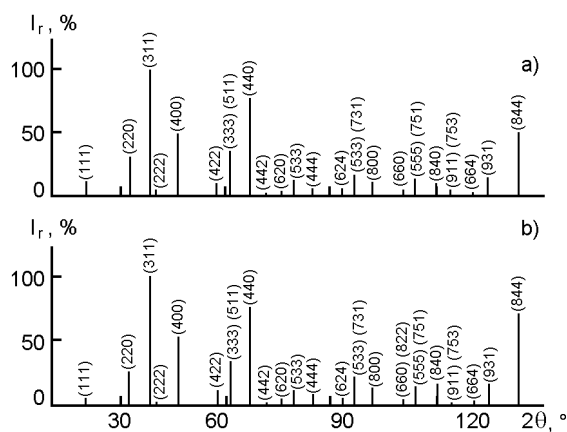


Fig. 3. Experimental (a) and calculated (b) diffraction patterns for spinel phase ($a = 7.9437 \text{ \AA}$). Cu $K\alpha_{1,2}$ radiation.

group) with the lattice period $a = 7.933$ to 7.948 \AA . This phase cannot be identified as one of the known cubic Al_2O_3 phases (γ , η , χ). The data on synthesis of such phases at high temperatures are also scarce. In [8], a f.c.c. phase ($a = 7.915 \text{ \AA}$) was found in the alumina reduction products with solid carbon and identified as AlAl_2O_4 , but no diffraction pattern is presented for the compound. In [9], the $\text{Al}[\text{Al}_{5/3}\square_{1/3}]\text{O}_4$ (η -alumina) compound has been reported to be synthesized at plasma deposition in reducing conditions. The compound has a spinel structure (Fd $\bar{3}m$ space group), $a = 7.906 \text{ \AA}$, but the presented diffraction pattern differs considerably from our results.

When constructing the model of spinel structure obtained in our experiments, the

Table 2. Structure data of spinel.

Atom	Position	Coordinates			Occupancy
		x	y	z	
Al	$8a$	0	0	0	0.67–1
Al	$16d$	0.625	0.625	0.625	1
O	$32e$	0.37(5)	0.37(5)	0.37(5)	1

experimental and calculated diffraction patterns for the variable composition structure (Fd $\bar{3}m$ space group, Table 2) were compared together. The occupancy of the $8a$ symmetry position equal to 0.67 answers to the $\text{Al}_{2.667}\text{O}_4$ (Al_2O_3) composition while the 1 one, to Al_3O_4 . The temperature factor was not taken into account in calculations. The calculation for that structure with the occupancy 1 (Al_3O_4 , see Fig. 3) gives a better agreement with experimental data than with 0.67 one (Al_2O_3). For the calculation using 30 lines, the R factor does not exceed 10 %.

The comparison of the proposed structure models for the new phases with the known corundum structure [10] has shown that using the models, it is possible to describe qualitatively the phase transformations observed (Fig. 4). As is seen in Fig. 4a, the oxygen positions in the (111) lattice plane within two layers coincide with the atomic positions within the (0001) plane of corundum lattice (1, 2), but an additional layer (3) is present in the spinel lattice. A similar picture is observed for the (001) plane of the H-phase hexagonal lattice and the (0001) plane of corundum, taking into account the rotation by 30° about the C axis

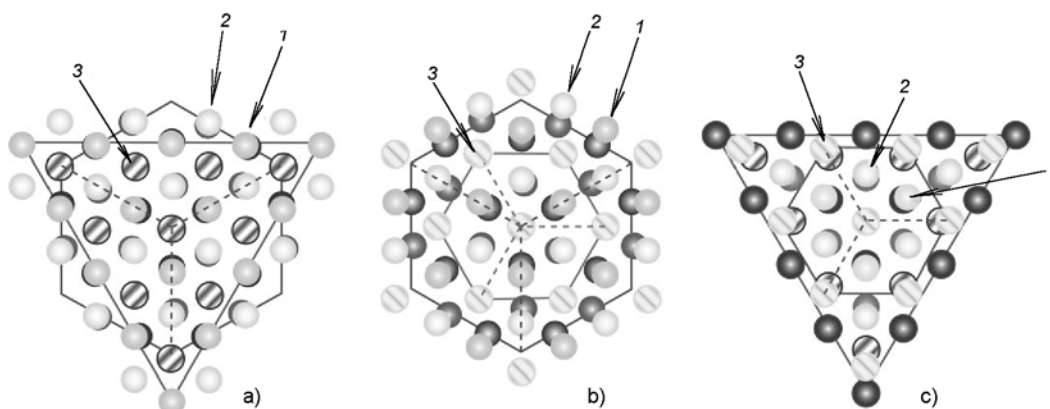


Fig. 4. Schemes of oxygen atomic arrangement in corundum (0001) and spinel (111) planes (a); corundum (0001) and H-phase (001) planes (b); H-phase (001) and spinel (111) planes (c). (a): 1, 2 — coincident positions (corundum, dark circles; spinel, light circles); 3 — "additional" layer in the spinel lattice (hatched circles). (b) 1, 2 — coincident positions (corundum, dark circles; H-phase, light circles); 3 — "additional" layer in the H-phase lattice (hatched circles). (c) 1, 2 — coincident positions (spinel, dark circles; H-phase, light circles).

revealed in experiment (Fig. 4b). The occupied positions (2c) of the H-phase hexagonal lattice coincide with the oxygen positions (1, 2) in the corundum lattice while the atoms of the additional layer (3) (the 2a positions occupied in part) occupy the Al atomic sites. All the oxygen positions in the H-phase and spinel lattices are coincident (Fig. 4c).

Comparing the above schemes, it can be concluded that the corundum \rightarrow H-phase \rightarrow spinel transition is realizable more easily than the direct corundum \rightarrow spinel one. In this case, it can be supposed that a stoichiometry distortion in the corundum lattice (resulting in increased distance between oxygen atoms) is accompanied by weakening and breakdown of O–Al bonds, so the Al atoms become displaced out of the positions thereof towards the oxygen layer, thus resulting in the lattice rebuilding into the H-phase structure. The consequent transition to the spinel structure may occur due to ordering of oxygen atoms in partially occupied sites. This supposition is confirmed indirectly by the observed dependence of the corundum-to-spinel conversion extent on the temperature and the atmosphere reducing potential. However, the possible direct corundum \rightarrow spinel transition cannot be excluded completely, the more so that layers free of H-phase (at the measurement sensitivity threshold level) were obtained in experiment. When so, it is to suppose that the phase differ in composition, the H-phase having a lower reduction extent, and its presence in the layer is defined by the homogeneity region of the spinel phase. It is to note that the experimental information obtained to date are still insufficient to determine unequivocally the stoichiometry of new phases. The better agreement between the experimental and calculated data for Al_3O_4 structure in the case of both H-phase and spinel means only that the compositions of those compounds is close to Al_3O_4 . This is evidenced also by the estimations of the absorbed oxygen amount at the back transition of the new phases into corundum at air annealing. Perhaps the observed lattice period variations are associated also with the variable composition of the phases.

An interesting feature of the observed structure and phase transformations consists in the genetic correlation between the new phases being formed and the initial corundum structure. This is observed both in experiment when the textured layers are studied and in analysis of the proposed structure models (Fig. 5). This correlation

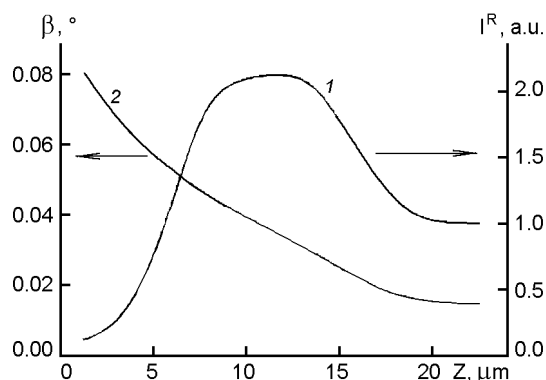


Fig. 5. Distribution profiles of the integral reflection intensity I^R (1) and the swinging curve integral width β (2) over the depth z of transformed corundum layer ((104) reflection, (0001) surface, $\text{Cu K}\alpha_1$ radiation).

follows also from consideration of changes in the single crystal substrate perfection in the course of reducing annealing. Fig. 5 presents the profile recovery results (2 μm step) of integral parameters obtained by asymmetric shooting (intensity I^R and width $\beta = I^R/I^m$ where I^m is the maximum ordinate value of the rocking curve) that characterize the structure perfection in depth. It is seen in the Figure that the formation of polycrystalline phases is accompanied by considerable distortions in the matrix near-surface layer resulting in increased β and I^R values as compared to the initial crystal state. The observed increase of I^R as depth increases to 10 μm is caused by appearance of a relief zone (where both polycrystalline phases are localized) during the near-surface layer transformation and characterizes the distribution of the reflecting substance within that zone. The subsequent drop in the $I^R(z)$ dependence is due to increasing structure perfection, and at $z > 20 \mu\text{m}$, the parameter takes the constant value inherent in bulk material.

Thus, the high-temperature annealing of $\alpha\text{-Al}_2\text{O}_3$ in a reducing atmosphere has been found to cause the corundum-to-spinel phase transformation. In the case of incomplete conversion, the transformed layer comprises a hexagonal phase, admittedly the variable composition compound $\text{Al}_2\text{O}_{3-x}$. The observed variations in the lattice parameters for both phases seems to be due to the variable composition thereof.

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Фазові перетворення $\alpha\text{-Al}_2\text{O}_3$ при відпалі у відновному середовищі

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Представлено результати досліджень трансформації структури корунду в результаті відпалу $\alpha\text{-Al}_2\text{O}_3$ в атмосфері Ar з відновними компонентами ($\text{CO} + \text{H}_2$) при температурі 1700–1900°C. Встановлено, що на поверхні монокристалічних зразків на фоні високої швидкості випару при відпалі утворюється полікристалічний шар, що містить нові фази. Одна з виявлених фаз відноситься до кубічної сингонії Fd3M (шпінель), інша — має гексагональну структуру (просторова група R63/mmc). Запропоновано якісну модель перетворення $\alpha\text{-Al}_2\text{O}_3 \rightarrow \text{AlAl}_2\text{O}_4$ (шпінель) за участю гексагональної фази.