Thermodynamic and experimental studies of the growth of magnesium-aluminum spinel crystals in molybdenum crucibles

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The possibility of crystal growth of magnesium-aluminium spinel $MgAl_2O_4$ from a melt under protective reducing gaseous media in molybdenum crucibles has been investigated. Thermodynamic estimates of the influence of the oxidizing potential of the atmosphere in the crystallization chamber on the composition of the gas phase of $MgAl_2O_4$, the processes of mass transfer, and the interaction of the dissociated products of $MgAl_2O_4$ with the crucible material have been carried out. The optimal composition of the protective atmosphere $(Ar + CO + H_2)$ and the technological parameters of the crystal growth of $MgAl_2O_4$ has been determined. Crystals of magnesium-aluminium spinel with a slight deviation from stoichiometry along the length of the crystal (molar ratio of Al_2O_3 to MgO from 1 to 1.3) were obtained by the horizontal directed crystallization method. The element analysis has shown that under the developed conditions it was possible to avoid significant contamination of crystals by the crucible material (Mo <=0.018 wt. %). The obtained results testify to the possibility of growing of $MgAl_2O_4$ crystals of optical quality without using expensive iridium crucibles.

Keywords: magnesium-aluminium spinel, $MgAl_2O_4$, crystal growth, horizontal directed crystallization, molybdenum crucibles.

Термодинамічні та експериментальні дослідження вирощування кристалів магній-алюмінієвої шпінелі у молібденових тиглях. *С.В.Ніжанковський, Н.С.Сідельнікова, О.О.Вовк, Ю.В.Сірик*

Досліджено можливості вирощування кристалів магній-алюмінієвої шпінелі $MgAl_2O_4$ з розплаву у захисному відновлювальному газовому середовищі з використанням тиглів з молібдену. Проведено термодинамічні оцінки впливу величини окислювального потенціалу атмосфери у кристалізаційній камері на склад газової фази $MgAl_2O_4$, процеси масопереносу та взаємодії продуктів дисоціації $MgAl_2O_4$ з матеріалом тигля. Визначено оптимальний склад захисної атмосфери $(Ar + CO + H_2)$ та технологічні параметри вирощування кристалів $MgAl_2O_4$. Методом горизонтальної направленої кристалізації одержано кристали $MgAl_2O_4$ з незначним відхиленням від стехіометрії за довжиною кристала (молярне відношення Al_2O_3 до MgO від 1 до 1.3). Елементний аналіз показав, що у розроблених умовах вдалося уникнути значного забруднення кристалів матеріалом тигля (Mo ≤ 0.018 мас.%). Отримані результати свідчать про можливість вирощування кристалів $MgAl_2O_4$ оптичної якості без використання дорого-вартісних іридієвих тиглів.

Исследованы возможности выращивания кристаллов магний-алюминиевой шпинели $MgAl_2O_4$ из расплава в защитных восстановительных газовых средах с использованием тиглей из молибдена. Проведены термодинамические оценки влияния величины окислительного потенциала атмосферы в кристаллизационной камере на состав газовой фазы $MgAl_2O_4$, процессы массопереноса и взаимодействия продуктов диссоциации

MgAl$_2$O$_4$ с материалом тигля. Определены оптимальный состав защитной атмосферы (Ar + CO + H$_2$) и технологические параметры выращивания кристаллов MgAl$_2$O$_4$. Методом горизонтальной направленной кристаллизации получены кристаллы MgAl$_2$O$_4$ с небольшим отклонением от стехиометрии по длине кристалла (молярное отношение Al$_2$O$_3$ к MgO от 1 до 1.3). Элементный анализ показал, что в разработанных условиях удалось избежать значительного загрязнения кристаллов материалом тигля (Mo ≤ 0.018 мас. %). Полученные результаты свидетельствуют о возможности выращивания кристаллов MgAl$_2$O$_4$ оптического качества без использования дорогостоящих иридиевых тиглей.

1. Introduction

Considerable research and practical interest in MgAl$_2$O$_4$ crystals are caused by peculiarities of their structure which provide the possibility to introduce activator (in particular, ions of transient metals), in combination with high chemical activity. chemical and thermal stability, high melting temperature and hardness, as well as the wide spectral interval of transmission of electromagnetic emission [1, 2].
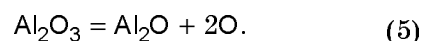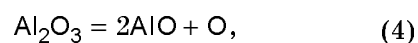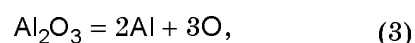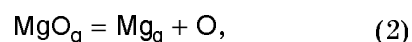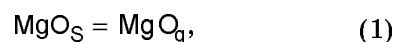
MgAl$_2$O$_4$ crystals are grown by different technologies such as the Verneuil [3, 4], float-zone [5, 6], micro-pulling-down μ-PD [7, 8] and Czochralski methods [4, 9–13]. Nowadays the last technology is mostly used for obtaining crystals with a diameter of ≥20 mm ($L \approx 50$–70 mm) and high optical and structural quality [13]. Due to the high melting temperature of the spinel (~ 2100°C), the growth technology requires the use of expensive crucibles made from Ir [10, 12, 13] or Ir–Re [7]. However, their operation/service temperatures are close to the melting temperature of iridium (2466°C) that essentially shortens the lifetime of the crucible and raises the cost of the growth process. In this connection, the development of iridium-free technology becomes a topical problem. In [14] there were reported the results of the growth of MgAl$_2$O$_4$ crystals (50 mm in diameter and 25 mm in length) with a composition close to the stoichiometric one. The crystals were obtained by the heat exchanger method (HEM) in protective Ar atmosphere using comparatively inexpensive Mo crucibles. However, in the aforementioned study, the spinel crystals of optical quality were not grown due to the formation of molybdenum and corundum inclusions in them.

The goal of the present work was to realize the thermodynamic analysis of the conditions for growing MgAl$_2$O$_4$ crystals in protective gaseous media and to study the phase, stoichiometric and impurity composition of the crystals obtained by the method of horizontal directed crystallization (HDC) using molybdenum crucibles.

2. Thermodynamic analysis

Preliminary estimations of the influence of the value of oxidation potential of the medium in the crystallization chamber on the composition of MgAl$_2$O$_4$ the gas phase, the processes of mass transfer and the interaction of the products of MgAl$_2$O$_4$ dissociation with the crucible material were based on studying vaporization thermodynamics of MgAl$_2$O$_4$.

As established in [15–18], evaporation of MgAl$_2$O$_4$ occurs mainly by heterogeneous reactions typical for evaporation of individual oxides:

$$MgO_S = MgO_g, \qquad (1)$$

$$MgO_g = Mg_g + O, \qquad (2)$$

$$Al_2O_3 = 2Al + 3O, \qquad (3)$$

$$Al_2O_3 = 2AlO + O, \qquad (4)$$

$$Al_2O_3 = Al_2O + 2O. \qquad (5)$$

According to the literature data [15–18], in the entire range of the compositions, except for the edge one (100 mol. % Al$_2$O$_3$), the gas phase over the system Al$_2$O$_3$–MgO mainly contains the three components — Mg, O$_2$, O, the concentration of the products of Al$_2$O$_3$ dissociation is essentially (more than by an order of magnitude) lower than that of MgO.

Changes in the gas phase composition over an oxide due to the mass transfer between the oxide and the environment can be illustrated through the volatility diagram [19] — the dependence of the value of equilibrium partial pressures of the dissociation products over the condensed oxide phase on the pressure of oxygen. Fig. 1 presents the results of the calculations of the composition of MgAl$_2$O$_4$ gas phase at changing:

$$P_{O_2} = P_O^2 \cdot (K^D O_2)^{-1}, \qquad (6)$$

$$P_{\mathsf{Al}} = \sqrt{P_{\mathsf{O}}^{-3} \cdot (K^D \mathsf{Al}_2 \mathsf{O}_3)}, \qquad (7)$$

$$P_{\mathsf{Al}_2\mathsf{O}_2} = P_{\mathsf{Al}}^2 \cdot P_{\mathsf{O}}^3 \cdot (K^D \mathsf{Al}_2\mathsf{O}_2)^{-1}, \qquad (8)$$

$$P_{\mathsf{AlO}} = P_{\mathsf{Al}} \cdot P_{\mathsf{O}} \cdot (K^D \mathsf{AlO})^{-1}, \qquad (9)$$

$$P_{\mathsf{Al}_2\mathsf{O}} = P_{\mathsf{Al}}^2 \cdot P_{\mathsf{O}} \cdot (K^D \mathsf{Al}_2\mathsf{O})^{-1}, \qquad (10)$$

$$P_{\mathsf{AlO}_2} = P_{\mathsf{Al}} \cdot P_{\mathsf{O}_2} \cdot (K^D \mathsf{AlO}_2)^{-1}, \qquad (11)$$

$$P_{\mathsf{Al}_2\mathsf{O}_3} = P_{\mathsf{Al}}^2 \cdot P_{\mathsf{O}_3} \cdot (K^D \mathsf{Al}_2\mathsf{O}_3)^{-1}, \qquad (12)$$

$$P_{\mathsf{MgO}} = K_{\mathsf{MgO}}^V, \qquad (13)$$

$$P_{\mathsf{Mg}} = K_{\mathsf{MgO}}^D \cdot P_{\mathsf{MgO}} \cdot (P_{\mathsf{O}})^{-1} \qquad (14)$$

In given calculations, the values of dissociation constants (K^D) and the reactions of congruent evaporations (K^V) were taken from [20, 21].

As seen from the diagram, the stoichiometric composition of $MgAl_2O_4$ corresponds to the minimum of the total pressure $P_O = P_{st}$. In the medium with $P_O \neq P_{st}$ there is observed nonstoichiometric evaporation and the shift of the vapor composition towards the decrease of $\sum P_O$ at $P_O < P_{st}$ and of $\sum P_{\mathsf{Al}}$, $\sum P_{\mathsf{Mg}}$ at $P_O > P_{st}$ (see Fig. 1). The dissociation equilibrium will be shifted up to achieving the stationary state characterized by equality of the ratios of the flows of gas-phase components and the stoichiometric coefficients of the compounds depending on external conditions (the oxygen potential of the medium and the temperature).

The partial pressure of oxygen in the gas phase over an oxide can be estimated using the balance ratios determined from the stoichiometric coefficients of the compound [22]. Since the main components of $MgAl_2O_4$ gas phase are Mg and MgO ([15–18], see Fig. 1), evaporation of $MgAl_2O_4$ can be described by the simplified balance equation which coincides with the equation for MgO evaporation:

$$\sum J_{\mathsf{O}} = \sum J_{\mathsf{Mg}}, \qquad (15)$$

where

$$\sum J_{\mathsf{O}} = J_{\mathsf{O}} + J_{\mathsf{O}_2} + J_{\mathsf{MgO}}, \qquad (16)$$
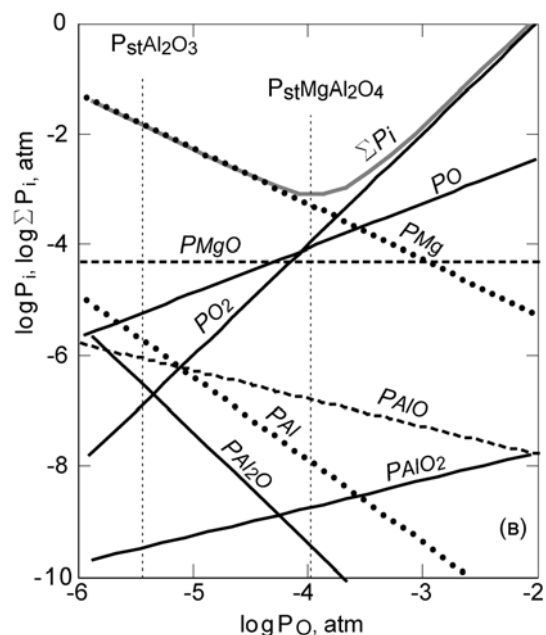
Fig. 1. Dependences of equilibrium partial pressures of P_i components and total pressure $\sum\limits_i P_i$ in $MgAl_2O_4$ gas phase on atomic oxygen pressure at $T = 2408$ K. P_{st} is atomic oxygen pressure in gas phase of stoichiometric AlV_2O_3 and $MgAl_2O_4$.

$$\sum J_{\mathsf{Mg}} = J_{\mathsf{Mg}} + J_{\mathsf{MgO}}. \qquad (17)$$

As shown in [23, 24], in the case when the medium over the condensed oxide phase (a raw material, a melt, growing crystal) contains reducing components, and while reduction of the oxide and its dissociation products CO and H_2 is thermodynamically probable, the oxygen of the oxide carries-over not only by own dissociation products containing oxygen but both by CO_2, H_2O and by the products of reducing reactions of the condensed oxide and gas-phase components under the interaction with CO and H_2. For $MgAl_2O_4$ such reactions are the following:
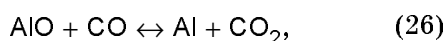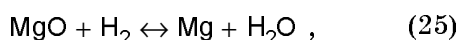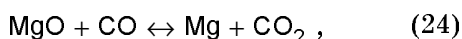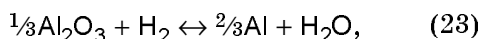
$$\mathsf{Al}_2\mathsf{O}_3 + \mathsf{CO} \leftrightarrow 2\mathsf{AlO} + \mathsf{CO}_2, \qquad (18)$$

$$\tfrac{1}{2}\mathsf{Al}_2\mathsf{O}_3 + \mathsf{CO} \leftrightarrow \tfrac{1}{2}\mathsf{Al}_2\mathsf{O} + \mathsf{CO}_2, \qquad (19)$$

$$\tfrac{1}{3}\mathsf{Al}_2\mathsf{O}_3 + \mathsf{CO} \leftrightarrow \tfrac{2}{3}\mathsf{Al} + \mathsf{CO}_2, \qquad (20)$$

$$\mathsf{Al}_2\mathsf{O}_3 + \mathsf{H}_2 \leftrightarrow 2\mathsf{AlO} + \mathsf{H}_2\mathsf{O}, \qquad (21)$$

$$\tfrac{1}{2}\mathsf{Al}_2\mathsf{O}_3 + \mathsf{H}_2 \leftrightarrow \tfrac{1}{2}\mathsf{Al}_2\mathsf{O} + \mathsf{H}_2\mathsf{O}, \qquad (22)$$

$$\tfrac{1}{3}Al_2O_3 + H_2 \leftrightarrow \tfrac{2}{3}Al + H_2O, \qquad (23)$$

$$MgO + CO \leftrightarrow Mg + CO_2, \qquad (24)$$

$$MgO + H_2 \leftrightarrow Mg + H_2O, \qquad (25)$$

$$AlO + CO \leftrightarrow Al + CO_2, \qquad (26)$$

$$Al_2O + CO \leftrightarrow 2Al + CO_2, \qquad (27)$$

$$AlO + H_2 \leftrightarrow Al + H_2O, \qquad (28)$$

$$Al_2O + H_2 \leftrightarrow 2Al + H_2O, \qquad (29)$$

$$CO + \tfrac{1}{2}O_2 \leftrightarrow CO_2, \qquad (30)$$

$$H_2 + \tfrac{1}{2}O_2 \leftrightarrow H_2O, \qquad (31)$$

$$H_2O + CO \leftrightarrow H_2 + CO_2. \qquad (32)$$
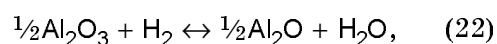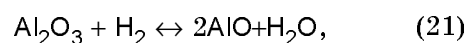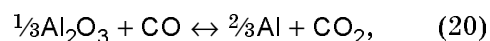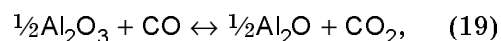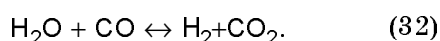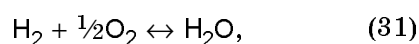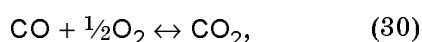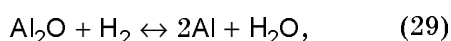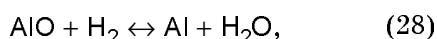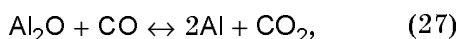
In this case:

$$\sum J_\delta^S = \sum J_O + J_{CO_2}^S + J_{H_2O}^S. \qquad (33)$$

where $\sum J_O$ is the sum of flows of the oxide dissociation products which contain O (16); $J_{CO_2}^S + J_{H_2O}^S$, the flows of the products of the reducing reactions of MgO and its dissociation products (24), (25), (30), (31).

Under the stationary conditions the flow of the dissociation products through the crystallization chamber medium (Ar, CO + H$_2$) can be described through the equation [30]:

$$J_i^S = \alpha \cdot b_i \cdot \left(P_i^0 - P_i^\infty \right), \text{ part. cm}^{-2} \cdot s^{-1}, \qquad (34)$$

where i is the vapor component (Mg, MgO, O, O$_2$, CO$_2$, H$_2$O); α, the accommodation coefficient;

$P_i^0 = P_i^S$, the pressure of the dissociation products over the oxide surface under the stationary conditions; P_i^∞, the pressure of the dissociation products outside the diffusion zone (in the calculations it was assumed that $P_i^0 > P_i^\infty$).

$$b_i = \left[(\beta_i^m)^{-1} + (\beta_{i-m}^d)^{-1} \right]^{-1}, \qquad (35)$$

where β_i^m and β_{i-m}^d are the kinetic coefficients of evaporation of the vapor components in molecular and diffusion mode:

$$\beta_i^m = (2\pi \cdot M_i \cdot R \cdot T)^{-1/2}, \qquad (36)$$

$$\beta_{i-m}^d = D_{i-m} \cdot (\delta \cdot R \cdot T)^{-1}, \qquad (37)$$

where M_i is the mass number of MgAl$_2$O$_4$ dissociation products (Mg, MgO, O, etc.); , the temperature, K; T, the diffusion coefficient of the particle (Mg, MgO, O, etc.) in the medium CO + H$_2$, Ar, Ar + CO + H$_2$, cm$^2 \cdot$s^{-1}; δ, the size of diffusion zone, cm.

In practice, the size of the diffusion zone, i.e. the distance at which the condition $P_i^0 > P_i^\infty$ is satisfied, is a real technological parameter and depends on the area of the melt, the area and temperature of the carbon-graphite heat shields, convective processes in the crystallization chamber, etc. [26]. Under real conditions, all the above-mentioned parameters are hardly controlled. In the calculations, the size of the diffusion zone was assumed to be less than or about the height of the sides of the crucible over the surface of the condensed phase (the raw material, the melt, the growing crystal) ($\approx 0.3{-}0.5$ cm).

At $\beta^m \ll |\beta^d$ Eq. (34) is transformed into the Hertz-Langmuir equation for the flow of particles, at $\alpha = 1$, it defines the maximum achievable theoretical rate of evaporation into vacuum. The pressure of the medium starts to influence the rate of evaporation when its value achieves the critical magnitude P^*. For evaporation of MgAl$_2$O$_4$ dissociation products in Ar medium the said value is $\sim 2{\cdot}10^{-3}$ torr [23]. When the pressure of the medium considerably exceeds P^*, the evaporation rate is limited by the diffusion of the vapor components through the medium.

The value of D_i was determined from the relation [32]:

$$D_{i-m} = \qquad (38)$$
$$= 1.8583 \cdot 10^{-3} \cdot \frac{T^{3/2}}{P_m \cdot \sigma_{i-m}^2 \Omega_D} \cdot \sqrt{(M_i)^{-1} + (M_m)^{-1}}$$

where $P_m \approx P(CO + H_2$, Ar, Ar + CO + H$_2$) is the total pressure of the medium, atm; σ_{i-m}, the intermolecular distance; Ω_D, the collision integral.

The values of σ_{i-m} and Ω_D were calculated using the reference data [26, 27].

At temperatures exceeding the melting point the accommodation coefficient $\alpha = 1$ [25], within the temperature interval 500–2300 K $\alpha \neq 1$, however, such a correction

does not result in essential changes in the calculation results.

P_O^S value is connected with P_{CO}, P_{H2}, $P_{CO_2}^S$ and $P_{H_2O}^S$ by the equilibrium constants of the reactions (30), (31), i.e.:

$$P_{CO_2}^S = P_O^S \cdot P_{CO} \cdot K_{CO_2}, \qquad (39)$$

$$P_{H_2O}^S = P_O^S \cdot P_{H_2} K_{H_2O}, \qquad (40)$$

where K_{CO_2} and K_{H_2O} are the constants of the said reactions.

Taking into account the above-mentioned parameters, the values of the dissociation constants of O_2 ($K_{O_2}^D$ and MgO (K_{MgO}^D and of the reaction of MgO K_{MgO}^V congruent evaporation [20, 21], Eq. (15) can be used to obtain the expression for calculation of the pressure of atomic oxygen in $MgAl_2O_4$ gas phase for the composition $MgO \cdot Al_2O_3$) under the stationary reducing conditions in the medium with preset values of partial pressure of the reducing CO and H_2 components:

$$A \cdot (P_O^S)^3 + B \cdot (P_O^S)^2 - C \cdot (P_O^S) - F = 0, \quad (41)$$

where

$$A = 2b_{O_2} \cdot (K_{O_2}^D)^{-1}, \qquad (42)$$

$$B = b_O + b_{CO_2} \cdot K_{CO_2} \cdot P_{CO} + \qquad (43)$$
$$+ b_{H_2O} \cdot K_{H_2O} \cdot P_{H_2},$$

$$C = b_{MgO} \cdot K_{MgO}^V \cdot K_{MgO}^D, \qquad (44)$$

$$F = b_{Mg} \cdot K_{MgO}^V \cdot K_{MgO}^D, \qquad (45)$$

In Fig. 2 the calculated pressures of atomic oxygen in $MgAl_2O_4$ gas phase under neutral conditions (Ar atmosphere, $P_{Ar} = 1$ atm), in $CO + H_2$ medium at/under a pressure of $\approx 0,5$ torr and in $Ar + CO + H_2$ gas mixture are compared with the tabulated data from [22] (curve *1′*) and the experimental data from [18] (curve *6*), obtained under the reducing conditions induced by the interaction of oxygen with the material of molybdenum effusion container.

The dependence of P_O^S on the total pressure of the medium (P_m), is insignificant (curves *3, 3′* in Fig. 2), and is defined predominantly by the change-over from mo-
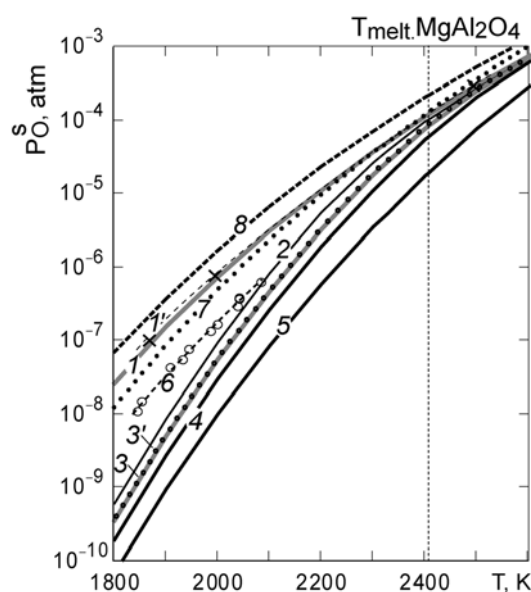

Fig. 2. Calculated values of partial pressure of atomic oxygen in $MgAl_2O_4$ gas phase under neutral conditions: *1* — $P_{Ar} = 1$ atm, *1′* — literature data [9], *2* — in Ar + CO medium, $P_{CO} = 0.5$ torr, *3* — in Ar + CO + H_2 medium, $P_{CO} = 0.5$ Torr, $P_{H2} = 0.1P_{CO}$, *3′* — in CO+H_2 medium, $P_{CO} = 0.5$ torr, $P_{H2} = 0.1P_{CO}$, *4* — in Ar + CO medium, $P_{CO} = 3$ torr, *5* — in Ar + CO + H_2 medium, $P_{CO} = 3$ torr, $P_{H2} = O_{CO}$, *6* — literature data [14].

lecular evaporation (when $b_i \approx \beta_i^m \sim M_i^{-1/2}$) to diffusion evaporation ($b_i \approx \beta_{i-m}^d \sim D_{i-m}$). At the same time, the dependence of P_O^S on the partial pressure of the reducing components of the medium is more essential, since it gives rise to a violation of $MgAl_2O_4$ stoichiometry related to oxygen.

Using the obtained values of P_O^S and (of) the corresponding dissociation constants, one can estimate the magnitudes of P_{Mg_S}, P_{MgO}^S, P_{Al}^S, P_{AlO}^S, $P_{Al_2O}^S$ from the expressions (6)–(14), and the corresponding flows of $MgAl_2O_4$ dissociation products from (34) (Fig. 3).

Correctness of the performed estimations can be believed by a good coincidence of the rate of $MgAl_2O_4$ evaporation calculated from the sum of the flows of dissociation and reduction products in the media with different compositions (for δ values on the order of the height of the crucible sides over the melt $\approx 0.3-0.5$ cm), with the experimentally obtained values of evaporation rate in the
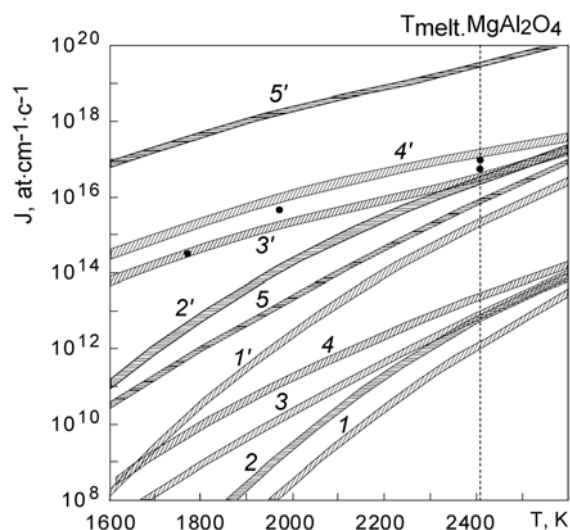
Fig. 3. Calculated values of flows of Al (1–5) and Mg (1′–5′) particles at evaporation of $MgAl_2O_4$ in the interval of $\delta \approx 0.3$–0.5 cm. 1, 1′ — in Ar + 20 % O_2, 2, 2′ — Ar, 3, 3′ — Ar+CO+H_2, $P_{CO} = 0.5$ torr, $P_{H2} = 0.1P_{CO}$, 4, 4′ — Ar + CO + H_2, $P_{CO} = 3$ torr, $P_{H2} = P_{CO}$ ($P_m = 1$ atm). 5, 5′ — in CO+H_2, $P_{CO} = 0.5$ torr, $P_{H_2} = 0.1P_{CO}$ ($Pm \approx 0,55$ torr). The points denote the experimental data obtained during evaporation of $MgAl_2O_4$ in Ar + CO +

medium Ar + CO + H_2, $P_{CO} \approx 0.5$–1 torr, $P_{H_2} \approx 0.1P_{CO}$ (shown by points in Fig. 3).

As follows from the obtained estimations, the presence of reducing components in the growth medium results in violation of the stoichiometry of $MgAl_2O_4$ related to oxygen and raises the evaporation rate. Consequently, it leads to a loss of Mg which is more essential than the one for neutral conditions and violation of $MgO \cdot Al_2O_3$ stoichiometry forward to Al_2O_3 with subsequent inhomogeneity of the composition of the crystal along its length. Under real crystallization conditions, the loss of Mg may reach 5–7 wt. % depending on the ratio of the geometric parameters (area — volume) of the melt and the crystallization time.

At the same time, the reducing conditions in the crystallization chamber that diminish P_O^S, allow weakening the intensity of mass transfer of the crucible material. This fact is confirmed by comparing the calculated values of the pressure of Mo oxidation to MoO_2 and MoO_3 condensed oxides (curves 7, 8 in Fig. 2) with the values of P_O^S in $MgAl_2O_4$ gas phase under different

reducing conditions (Curves 1–5). The pressure of oxygen necessary for the formation of MoO_3 is higher than the one in $MgAl_2O_4$ gas phase even under neutral conditions. MoO_2 can be formed under neutral conditions. Under the reducing conditions when the pressure of the reducing component exceeds 0,5 torr the partial pressure of oxygen in $MgAl_2O_4$ gas phase becomes lower in comparison with the one necessary for the formation of MoO_2.

The performed estimations allow determining the optimal composition of the reducing atmosphere that makes it possible to diminish the intensity of mass transfer for the crucible material and, at the same time, not to lead to essential violation of $MgAl_2O_4$ stoichiometry. The real technological crystal growth parameters were established experimentally taking into account these estimations.

3. Experimental

$MgAl_2O_4$ crystals with the dimensions 110×70×20 mm were grown by the method of HDC [23, 28] in the protective atmosphere based on the mixture of argon and the reducing additions CO and H_2 under a total pressure of ~ 1 atm. As an initial raw material, there was used $MgAl_2O_4$ powder (99.7 wt%, 0.3 wt. % of Al_2O_3, Baikowski), sintered in the form of tablets at 1500°/4 h.

The impurity composition of the grown crystals was studied by the method of inductive coupled plasma-atomic emission spectroscopy.

For X-ray phase analysis there was used a diffractometer Siemens D500 (CuKα radiation, graphite monochromator, $\Theta - 2\Theta$ geometry, point scintillation detector $5° \le 2\Theta \le 110$, $\Delta 2\Theta = 0.02°$).

The quantities of magnesium and aluminum for stoichiometric calculations were determined by direct complexometric titration in alkaline medium with a dark blue acid chrome indicator. For elimination of interfering influence of aluminum there was used triethanolamine. The content of aluminum was determined by reverse complexometric titration using the solution of cuprum dichloride in acetate medium with 1-(2-pyridylazo)-2-naphthol used in the capacity of an indicator. The stoichiometry of the crystals was estimated using the coefficient x ($MgO \cdot xAl_2O_3$) corresponding to the molar ratio of Al_2O_3 to MgO.
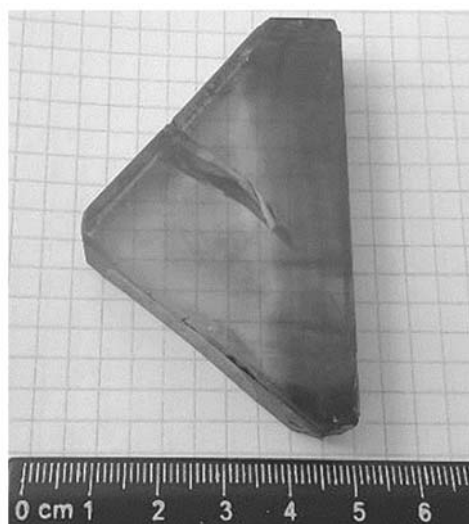
Fig. 4. The part of MALO crystal 2 of optical quality grown by HDC method.

4. Results and discussion

$MgAl_2O_4$ crystals were obtained under the same growth conditions (the temperature regime, the composition of the gas medium), but at different crystallization rates v: 3 mm/hr (crystal 1) and 8 mm/h (crystal 2). The grown crystals were shaped like rectangles with dimensions up to 110×70×20 mm. The initial part of the crystal (~ 30 mm) of a characteristic yellow-brown color was transparent and did not contain visible inclusions and light-scattering centers (Fig. 4), whereas the remaining part was turbid.

Fig. 5 presents the typical XRD patterns of the transparent part of the crystal. The composition corresponds to the magnesium-aluminum spinel $MgAl_2O_4$ with the cubic structure of *Fd3m* symmetry. The analysis of the turbid part of the ingot revealed an extra phase of Al_2O_3 in the form of corundum with *R3c* symetry.

The performed analysis of the content of magnesium and aluminum in the crystals shows that for both crystals there occurs violation of the stoichiometry along their length (from the "nose" to the "tail") due to magnesium depletion. The composition of such non-stoichiometric spinel crystals is described by the general formula $MgO·xAl_2O_3$, where $x > 1$. Thereat, with a lower crystallization rate, the loss of magnesium is essentially more sufficient, and the intensity of evaporation from the melt is higher. For crystal 1 (v = 3 mm/h) the coefficient x increases along the crystal length from 1.1 to 1.88 (Fig. 6, line *1*). For
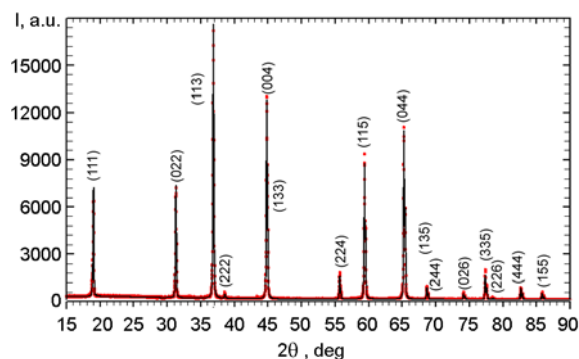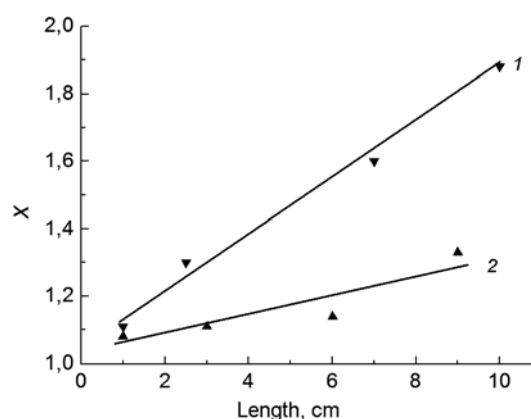

Fig. 5. XRD pattern of $MgAl_2O_4$ crystal.

Fig. 6. Distribution of the coefficient x over the length of $MgO·xAl_2O_3$ crystals grown at crystallization rates : *1* — 3 mm/hr, *2* — 8 mm/hr.

Table 1. Distribution of crystal lattice parameter a and of coefficient x along the length of $MgO·xAl_2O_3$ crystal grown at 8 mm/h crystallization rate

Distance from crystal "nose", cm	Coefficient x	Lattice parameter a, Å
1	1.08	8.08258(8)
3	1.11	8.07942(11)
6	1.14	8.06520(13)

Crystal 2 (v = 8 mm/hr) x grows from 1.08 to 1.3 (Fig. 6, Line 2).

As the spinel stoichiometry violation rises, the crystal lattice parameters decrease. For Crystal 2 the increase of x from 1.08 to 1.14 the parameter a grows from 8.08258(8) to 8.06520(13) Å (Table 1).

In the stoichiometric spinel $MgAl_2O_4$ Mg^{2+} ions occupy the tetra positions, whereas Al^{3+} ions are located in the octahedral environment. If the stoichiometry violation is caused by the loss of magnesium,

Table 2. Results of impurity analysis of MgO·xAl$_2$O$_3$ crystal

Content of element, wt.%					
Co, W, V	Ba, Cr	Cu, Mn	Cd	Ni	Pb
<5·10^{-4}	<5·10^{-3}	<2·10^{-4}	<1·10^{-4}	<2·10^{-3}	0.001−0.018

some Al^{3+} ions are transferred to the formed tetrahedral vacancies. Thereat, for charge compensation, there are formed octahedral vacancies [29, 30]. Since the radius of Al^{3+} in the tetrahedral position $(r(Al^{3+}_{IV}) = 0.39$ Å) is essentially smaller than Mg^{2+} radius $(r(Mg^{2+D}_{IV}) = 0.57$Å), such substitution diminishes the lattice volume and, consequently, its parameter.

The element analysis of Crystal 2 shows a low content of the impurities (Table 2). The content of molybdenum in different parts of the crystal ranges from 0.001 to 0.018 wt%. The maximum concentration is observed in the near-surface part of the crystal. This confirms the idea that the basic contribution to the contamination of the crystal by the crucible material is caused by the volatile oxides that resulted in oxidation of crucible material followed by their transfer to the surface of melt [23].

5. Conclusions

There were performed thermodynamic estimations of the influence of the value of the oxidative potential of the atmosphere in the growth chamber on the composition of MgAl$_2$O$_4$ in the gas phase, as well as on the processes of mass transfer and interaction of MgAl$_2$O$_4$ dissociation products with the crucible material (molybdenum).

Such estimations allowed to establish the optimum composition of the protective atmosphere (Ar + CO + H$_2$) and the technological parameters of the growth of MgAl$_2$O$_4$ crystals by the method of HDC. That made it possible to lower the intensity of molybdenum mass transfer and to prevent an essential violation of MgAl$_2$O$_4$ stoichiometry. The crystals with the composition corresponding to that of MgAl$_2$O$_4$ magnesium-aluminum spinel with the cubic structure of *Fd3m* symmetry were obtained. Along the length of the crystals, there was observed insignificant deviation from the stoichiometric composition (up to $x \sim 1.3$) caused by partial evaporation of magnesium oxide. The initial part of the crystal was transparent, without both visible inclusions and light-scattering. The element analysis showed that this did not lead to consider-

able contamination of the crystals by the crucible material (Mo≤0.018 wt%).

Thus, the obtained results prove the possibility of the growth of magnesium-aluminum spinel crystals of optical quality from the melt without using expensive iridium crucibles in protective gaseous media. Further improvement of the parameters of crystals requires a more detailed study of the structure, optical properties of crystals and optimization of the technological conditions.

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