

UDC 666.7:546.05

## PECULIARITIES OF SOL-GEL SYNTHESIS OF ALUMINUM-MAGNESIUM SPINEL

F. G. Khomidov,<sup>1</sup> Z. R. Kadyrova,<sup>1,2</sup> Kh. L. Usmanov,<sup>1</sup> Sh. M. Niyazova,<sup>1</sup> and B. T. Sabirov<sup>1</sup>

Translated from *Steklo i Keramika*, No. 6, pp. 48 – 52, June, 2021.

The results of studies of the chemical and mineralogical characteristics of alumina-containing wastes of the gas processing industry and the possibilities of their use for the synthesis of aluminum-magnesium spinel are presented. The optimal condition for the synthesis of  $MgAl_2O_4$  spinel by the sol-gel method using alumina-containing waste is found to be 1000°C temperature and 120 min soaking.

**Key words:** aluminum-magnesium spinel, sol-gel method, alumina-containing waste, phase transformations, x-ray phase analysis,  $\gamma$ -aluminum oxide-aluminum.

Magnesium spinel  $MgAl_2O_4$  is an important functional material. Due to its high chemical inertness, unique thermomechanical and optical properties, and high melting point (2135°C) is of great importance as a dopant and semitransparent optical and special highly refractory material for modern technology [1 – 4]. Spinel is mainly an essential component of refractory materials for lining steel-smelting ladles in metallurgy, transition and combustion zones of cement rotating and regenerators of glass-melting furnaces [5].

In industry, more than 70 – 80% of  $MgAl_2O_4$  spinel is produced by the solid-phase reaction method. The synthesis of spinel requires homogeneous, highly reactive, and non-agglomerated powders of the starting components with firing temperature  $> 1600^\circ C$ , which is necessary in order to achieve complete spinelization by means of solid-phase reactions. Consequently, high-temperature firing promotes grain growth and solid agglomeration of aluminum-magnesium spinel powders [6].

Many methods for synthesizing aluminum-magnesium spinel nanopowder have been developed and used in the last decades, including hydrothermal methods [7], combustion synthesis [8], lyophilization [9], Pechini method [10], and precipitation [6] as well as the sol-gel method [3, 11]. It should be noted that, year after year, a decrease in the synthesis temperature of  $MgAl_2O_4$  spinel becomes a very real problem.

Since the sol-gel method makes it possible to form the necessary phase compositions and structure of the material at lower temperatures, the results of the synthesis of aluminum-magnesium spinel powder by the sol-gel method using alumina-containing waste from the gas processing industry are presented here. Along with temperature reduction the sol-gel method promotes lower consumption of primary native raw materials and less environmental pollution.

The chemical reagents magnesium nitrate hexahydrate  $Mg(NO_3)_2 \cdot 6H_2O$  (chemically pure grade) and an alumina-containing spent catalyst from the gas processing industry were used as a source of cations. Nitric acid  $HNO_3$  (chemically pure grade) was used as a solvent, citric acid monohydrate as a chelating and polymerizing agent, and distilled water as a hydrolyzing agent.

X-ray phase analysis (LABX XRD-6100 SHIMADZU diffractometer,  $CuK_\alpha$  radiation,  $\beta$ -filter-Ni, wavelength 1.5418 Å, tube current and tube 30 mA, 30 kW) was used to identify the phase composition of the components used and the samples obtained. The constant rotation speed of the detector was equal to 4 deg/min with  $0.02^\circ$  steps ( $\omega/2\theta$  – mesh) and the scanning angle varied from 4 to  $80^\circ$ . For all samples, the scans were conducted under constant conditions. The international handbooks of x-ray powder diffraction patterns were used in the calculations and to identify phases [12].

In practice, the Claus method is used to purify natural gas from hydrogen sulfide. In particular, at the Shurtan Gas Chemical Complex (SGCC) in Uzbekistan catalytic oxida-

<sup>1</sup> Institute of General and Inorganic Chemistry, Academy of Sciences of Uzbekistan, Tashkent, Uzbekistan.

<sup>2</sup> E-mail: kad.zulayho@mail.ru.

**TABLE 1.** Results of Chemical Analysis of Alumina-Containing Spent Catalyst Before and After Heat Treatment

Component	Weight content of oxides, %								LOI, %
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub> total	TiO <sub>2</sub>	MgO	CaO	R <sub>2</sub> O	SO <sub>3</sub> total	
Initial catalyst SGCC	0.46	82.20	0.04	0.09	1.15	1.23	0.43	0.10	14.15
Calcined catalyst SGCC	0.54	96.02	0.05	0.11	1.34	1.44	0.50	–	–

**Note.** Loss on ignition (LOI) includes: hygroscopic, constitutional, and crystallization water as well as organic and volatile substances and CO<sub>2</sub>.

tion of the latter by atmospheric oxygen is conducted on the surface of high-alumina ‘bauxitic’ catalyst with ‘gaseous’ sulfur obtained as a byproduct. High-porosity synthetic granular aluminum hydroxide is used as a catalyst, which, when operating at 400°C and above, partially dehydrates to the oxide  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Table 1). The weight content of Al<sub>2</sub>O<sub>3</sub> in this product is equal to 82–90%, and after calcination at 900°C usually reaches at least 95% [13–15].

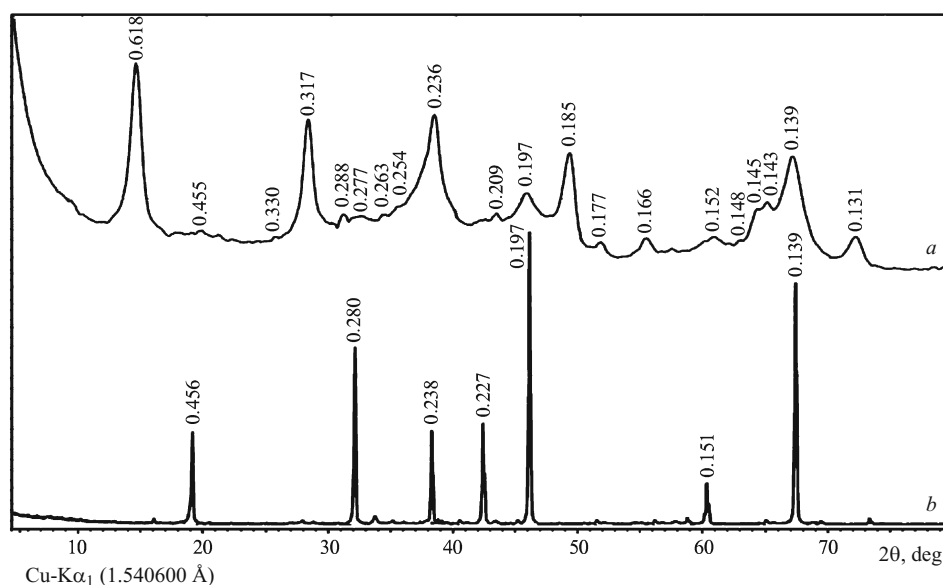
X-ray phase analysis showed that the mineralogical composition of the original spent catalyst includes gibbsite minerals with interplanar distances  $d = 0.618, 0.317, 0.241, 0.185, 0.145, 0.143,$  and  $0.131$  nm and gamma alumina with  $d = 0.455, 0.288, 0.236, 0.226, 0.197, 0.152,$  and  $0.139$  nm (Fig. 1a).

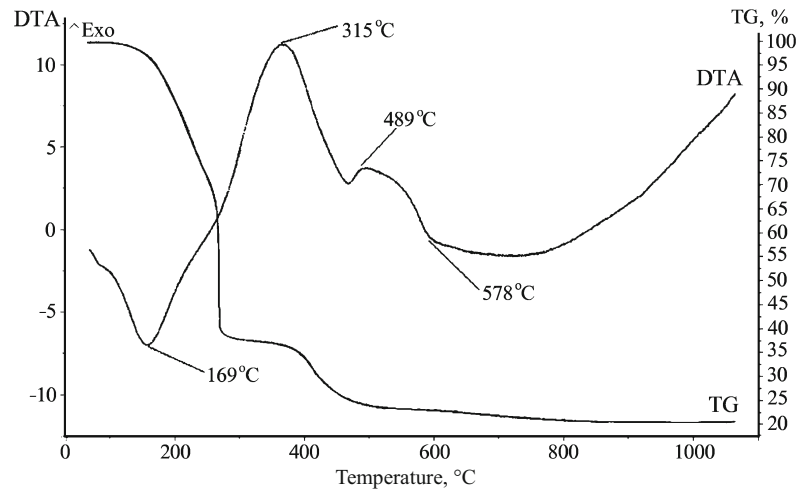
To increase the content of single-phase Al<sub>2</sub>O<sub>3</sub> the alumina-containing waste was heat treated at 900°C with 120 min soaking. As a result, aluminum oxide was obtained in the  $\gamma$ -form, which crystallizes in a cubic structure. The x-ray diffraction patterns of the samples show that the lines of diffraction maxima corresponding to the mineral Al<sub>2</sub>O<sub>3</sub> were found after the alumina-containing waste underwent heat-treatment:  $d = 0.456, 0.280, 0.238, 0.227, 0.197, 0.151,$

and  $0.139$  nm (Fig. 1b); the diffraction peaks corresponding to the gibbsite minerals vanish due to dehydration.

The results of thermogravimetric and differential thermal analysis indicate that weight loss is observed mainly at a temperature of 150–615°C. The differential thermal analysis of samples of alumina-containing waste showed (Fig. 2) that the heating curve of the sample contains two endothermic effects — at 169 and 578°C — associated with the removal of H<sub>2</sub>O molecules. The two exothermic effects appearing at 315 and 489°C are due to the oxidation and burn-out of organic substances, as well as the recrystallization of gibbsite to boehmite  $\gamma$ -AlO(OH).

The second weight loss associated with the endothermic peak at 578°C is explained by the crystallization of boehmite into  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (as seen in the x-ray diffraction pattern in Fig. 1). Weight loss occurs by the reaction  $2\text{AlOOH} \rightarrow \text{Al}_2\text{O}_3 + \text{H}_2\text{O}$  by removing the H<sub>2</sub>O molecule, which is accompanied by the appearance of thermal effects due to weight reduction. According to the thermogravimetric curve the total weight loss in the temperature range 150–615°C is 14.2%. No thermic event is observed on raising the temperature to 1100°C.

**Fig. 1.** X-ray diffraction patterns of alumina-containing waste: a) initial; b) heat treated at 900°C.

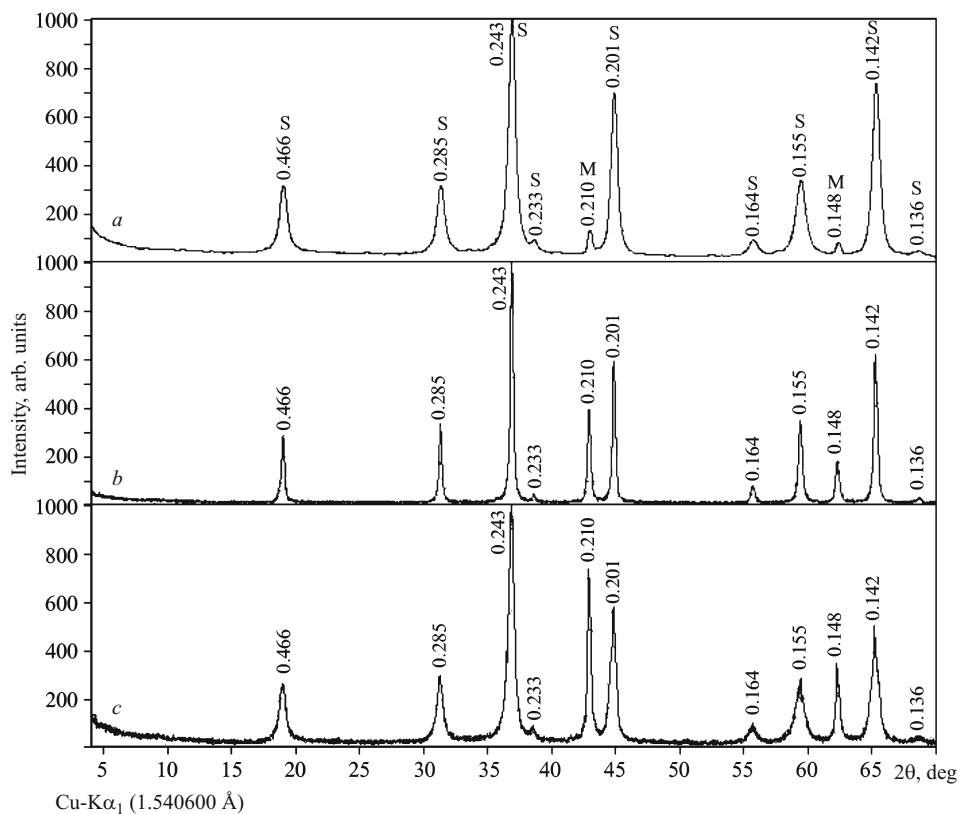


**Fig. 2.** Results of thermogravimetric TG and differential thermal analysis DTA of alumina-containing waste.

The resulting  $\gamma$ -form of aluminum oxide was comminuted in an agate mortar to the microlevel (0.7 – 1.0  $\mu\text{m}$ ), dissolved in distilled water, and acidified with nitric acid  $\text{HNO}_3$ . Magnesium nitrate hexahydrate  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was dissolved in distilled water. The resulting solutions were stirred at room temperature, after which citric acid was added and then stirred with a magnetic stirrer at 70 – 80°C until a gel-like mass was obtained. The resulting gel was dried at 125°C in an SNOL 3.5/350 drying oven for 8 h.

The dried gel was kept at 1000°C for 30, 60, and 120 min in order to determine the formation of the structure of crystalline magnesium aluminate and the effect of the soaking time during heat treatment on the process of synthesis of magnesium aluminum spinel, obtained by the sol-gel method, and full completion of the formation of the spinel crystal structure (Fig. 3).

The x-ray diffraction patterns show that the most intense effects of diffraction lines appear near grazing angle  $2\theta$



**Fig. 3.** X-ray diffraction patterns of isothermally processed synthesized samples at 1000°C, held for a) 30 min; b) 60 min; c) 120 min.

**TABLE 2.** Indexing of the X-Ray Diffraction Pattern of Spinel Powder and Comparison with a Standard X-Ray Diffraction Pattern According to ICPDS Data

Samples synthesized at 1000°C with different soaking times				Spinel, according to ICPDS data (5–0672)		
$d$ , Å	$I$ , % (30 min)	$I$ , % (60 min)	$I$ , % (120 min)	hkl	$d$ , Å	$I$ , %
4.665	24	28	29	111	4.670	4
2.853	26	31	31	202	2.858	40
2.431	100	100	100	311	2.436	100
2.331	5	5	9	222	2.333	13
2.017	58	60	68	400	2.021	58
1.641	6	7	9	422	1.649	10
1.553	26	29	31	511.333	1.555	45
1.420	44	61	72	404	1.429	58
1.361	3	3	4	531	1.368	5

(36.9, 44.5, and 65.3°) in all samples at three soaking intervals (see Fig. 3).

These diffraction lines with interference indices hkl (311), (400), and (404) correspond to the magnesium aluminate phase. However, for the soaking times 30 min (Fig. 3a) and 60 min (Fig. 3b) a high intensity  $I$  is observed for the diffraction lines  $d = 0.210, 0.248$  ( $2\theta = 42.9; 62.4^\circ$ ), corresponding to magnesium oxide that do not participate in the spinel phase transformation. However, on increasing the soaking time to 120 min these lines diminish, resulting in an intensification of the diffraction lines  $d = 0.466, 0.285, 0.233, 0.201, 0.164, 0.155,$  and  $0.142$  nm, corresponding to spinel (Table 2). This confirms that the formation of the spinel crystal structure is fully complete.

It should also be noted that diffraction lines corresponding to the  $\gamma$ -form of aluminum oxide are not observed in the x-ray diffraction patterns of samples fired to 1000°C, which indicates that it reacts actively as compared with magnesium oxide.

In summary, the possibility of low-temperature synthesis of a fine powder of aluminum-magnesium spinel by a sol-gel method using alumina-containing waste, magnesium nitrate, and citric acid was investigated. It was found that at 400°C the citrate precursors decompose and the formation of aluminum-magnesium spinel commences. In addition, the completion of the reactions leading to the formation of cubic crystalline phases of aluminum-magnesium spinel is due to heat treatment of the prepared mixture at 1000°C with 120 min soaking.

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