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Influence of heat treatment mode of various magnesia rocks on their properties

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Abstract

Investigations of the changes of structure, specific surface and true density of following high-magnesia rocks at heat treatment have been performed: brucite rocks, magnesite, hydromagnesia rocks, amorphous magnesite. It has been revealed that to obtain chemically active magnesium oxide, which is used for synthesis of high-refractory materials and obtaining magnesia binder, it is necessary to burn at low or moderate temperatures in the temperature range of 500-800 °C. Increase of temperature more than 800 °C leads to obtaining densely sintered cubic magnesium oxide with the periclase structure.

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Keywords: structure; heat treatment; brucite; magnesite; hydromagnesite; amorphous magnesite; true density; specific surface

1. Introduction

Magnesia powders which composition corresponds to magnesium oxide (MgO) with small amount of admixtures are obtained on the basis of magnesia raw materials. In dependence on conditions of heat treatment and quality of initial raw materials the powders have various physical and physical – chemical properties and, correspondingly, are used in various branch of industry.

The most mass product of processing magnesia row material is magnesite, "dead" burned at temperature more than 1000 °C; its share is 70 – 75 % of world production of magnesia powders. Share of caustic magnesite is 25-30%, to obtain it magnesia raw material are burned at temperature of 600-800 °C, one of fused periclase, obtained by means of burning up to sintering at 1600 – 1650 °C or by electric melting of natural magnesia materials, is 3-5%[1].

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Use of magnesia materials is defined by its properties acquired in process of heat treatment. It is known, for example, that driving force of sintering process is difference of free surface energies of powder and compact materials, and surface energy value is proportional to the powder specific surface. Periclase powders which passed high temperature treatment and have dense periclase structure are used to obtain high quality refractories for lining industrial high temperature furnaces of steel industry. Heat treatment in limits of 500-800 °C suppose obtaining high active magnesium oxide being able to interact with water and various other matters that defines its use as the main component at obtaining refractory concrete and building materials.

Change of physical and physical – chemical properties at heating natural magnesia materials is of great importance for synthesis of new phases at obtaining end products such as magnesia, chromo - magnesia and spinel-like refractory materials as well as composite materials of building purpose with set of unique properties [2, 3].

Basing on the above mentioned, in the process of performance of this work we investigated character of change of the main physical and physical – chemical properties of initial magnesia materials at their heat treatment: true density, specific surface as well as transformation of phase composition in process of burning the main kind of high magnesia raw materials.

2. Objects and methods of investigations

High magnesia rocks, which are traditionally used as magnesia component of row material mixtures of refractory and building materials are used as objects of investigation . This large crystalline magnesite $MgCO_3$ of Savinski deposit (Irkutskaya oblast), amorphous magnesite $MgCO_3$ and hydromagnesia rock of Khalilovski deposit (Orenburgskaya oblast) and brusite $Mg(OH)_2$ of Kuldurski deposit (Evreyskaya autonomic oblast). Chemical and mineralogical composition of magnesia rocks is presented in Table 1.

Savinski magnesites represent large crystalline rocks with radial – radiant “stellar” texture. Impurity rocks may be represented with fine – graded dolomite, talc, chlorite, quartz, pyrite but they, mainly, are primary dolomites, that is confirmed with X-ray phase analysis[1].

Khalilovski magnesite is represented by amorphous form i. e. crystalline structure is found only under a microscope. Khalilovski deposit is characterized by presence of serpentinous magnesites. Hydromagnesite is formed at weathering of ultra-basic rocks - magnesites, lays down veinlets and rings in serpentinites. Finding higher (up to 9.86 wt. %) content of silica in chemical composition of magnesia rocks of Khalilovski deposit is explained by presences of serpentinites rocks.

Table 1. Chemical composition of magnesia rocks.

Magnesia rocks	Content of oxides, wt. %								Mineral composition
	MgO	SiO_2	Al_2O_3	CaO	Fe_2O_3	MnO	$\Delta m_{пр}$	Total	
Large crystalline magnesite of the Savinski deposit	46.88	1.60	0.59	0.85	0.80	0.29	50.26	101.27	Magnesite $MgCO_3$ Dolomite $MgCO_3 \cdot CaCO_3$
Amorphous magnesite of Khalilovski deposit	48.22	6.16	0.09	2.33	1.03	0.05	43.12	101.00	Magnesite $MgCO_3$ Clinochrysotile $Mg_3Si_2O_5(OH)_4$
Hydromagnesia rock of Khalilovski deposit	43.32	9.86	0.69	0.52	1.17	0.029	45.33	100.91	Hydromagnesite $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ Dypingite $Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$ Nesquehonite $Mg(HCO_3)(OH) \cdot 2H_2O$ Clinochrysotile $Mg_3Si_2O_5(OH)_4$
Brusite of Kuldurski deposit	63.91	1.90	2.00	1.06	0.19	-	30.94	100.00	Brusite $Mg(OH)_2$ Dolomite $MgCO_3 \cdot CaCO_3$ Clinochrysotile $Mg_3Si_2O_5(OH)_4$

Mineral brusite represents magnesium hydroxide $Mg(OH)_2$. Kuldurski deposit is represented by three kinds of texture - structure types of brucites: pseudomorphous (fibrous – grained), colloform (fibrous – banded), and

automorphous (lamellar – grained). Impurity minerals in brucite rocks are presented by dolomite, calcite and serpentinite.

Heat treatment of preliminary fine grained magnesia rock samples was performed at temperatures of 400, 500, 600, 700, 800, and 1000 °C with exposure at end temperature during 1 hour. True density and specific surface of burned samples as well as their behavior at heating were defined after heat treatment.

In the course of investigations we have carried out thermoanalysis (TGA/DTA) with help of thermoanalyzer for synchronous thermoanalysis NETZSCH STA 449 F3 Jupiter. Investigation was carried out up to temperature of 1000 °C in air media in the Center of management of scientific – research equipment of Tomsk polytechnic university.

Determination of specific surface of caustic magnesia powders was performed by method of low temperature adsorption of nitrogen using BET-analyzer of specific Quantachrome NOVA 2200e. High values of specific surface are connected with influence of this indicator not only on particle sizes, but also on imperfections of their surface and structure.

True density was determined by pycnometric method[4].

3. The results of investigation and their discussion

The results of thermal analysis of magnesia rock samples showing temperatures of phase transitions in course of increasing temperature are presented in fig. 1, 2, 3, 4. Dependencies of change of specific surface and true density on temperature of heat treatment of magnesia rock samples are shown in figure 5.

3.1. Brucite

At ignition of brucite rocks the main effect is observed at temperature of 410.9 °C (Fig. 1), that corresponds to process of dehydration of brucite $Mg(OH)_2$. Burning of brucite at temperature of 400-500 °C leads to formation of high active magnesium oxide with defect structure with specific surface of 114-117 m^2/g (fig. 5, a). In addition,

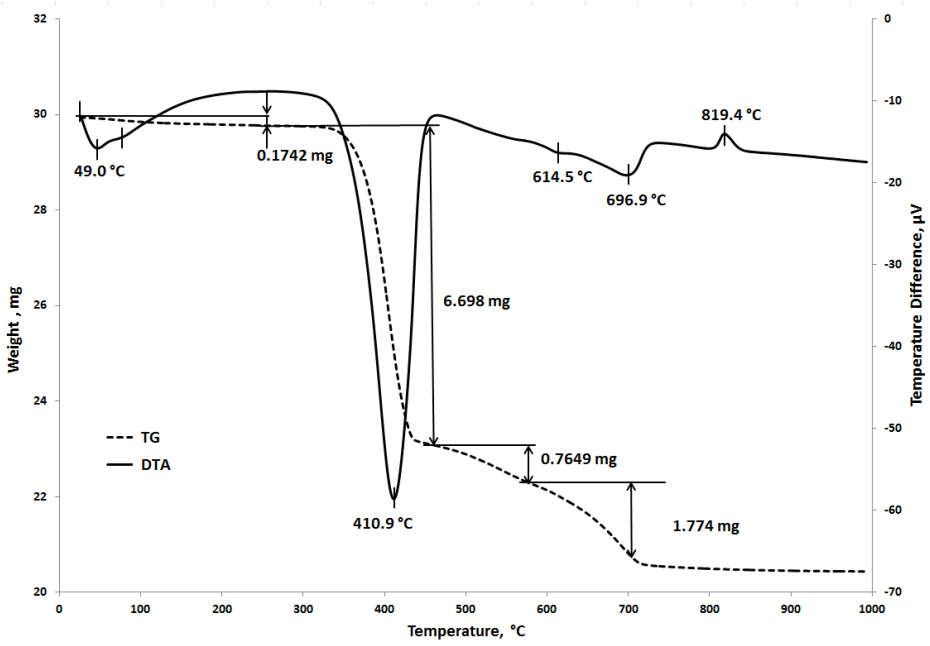

Fig. 1 Thermogram of brucite

there are two small endothermic effects at 614.5 and 696.9 °C, which correspond to decarbonization of impurity magnesite $MgCO_3$ and dolomite $MgCO_3 \cdot CaCO_3$ on the thermogram. Exothermic pick with maximum at 819.4 °C

shows that brucite rock contain minute amount of clinochrysotile which transfers in forsterite at this temperature. Increase in the temperature more than 500 °C leads to increase of true density values to 3.05 g/cm^3 at the temperature of 1000 °C and to decrease of specific surface down to 31.1 m^2/g (1000 °C). It is connected with improvement of structure of MgO crystals, their densification and increase of sizes.

3.2. *Amorphous magnesite*

Heat treatment of amorphous magnesite leads to formation of high active magnesium oxide with defect structure that corresponds to endothermic effect at temperature of 579.2 °C (fig. 2). Also, decarbonization of larger particles of $MgCO_3$ takes place at temperature of 702.3 °C. Temperature of 817.1 °C, at which one observes exothermic pick, corresponds to temperature of recrystallization of clinochrysotile in forsterite. Decarbonization of amorphous magnesite in temperature range from 500 to 700 °C leads to formation of high active free magnesium oxide with defect structure which is confirmed by the higher values of specific surface up to 48.5 m^2/g and low values of true density 2.69 g/cm^3. It is necessary to note that obtaining active, so named, caustic magnesium oxide from amorphous magnesite takes place at the lower temperatures (500-700 °C) in comparison with coarse – crystalline magnesite (600-800 °C). It is connected with peculiarity of amorphous magnesite structure, which has cryptocrystalline character with small crystals that allows to perform decarbonization of amorphous $MgCO_3$ particles at lower temperature.

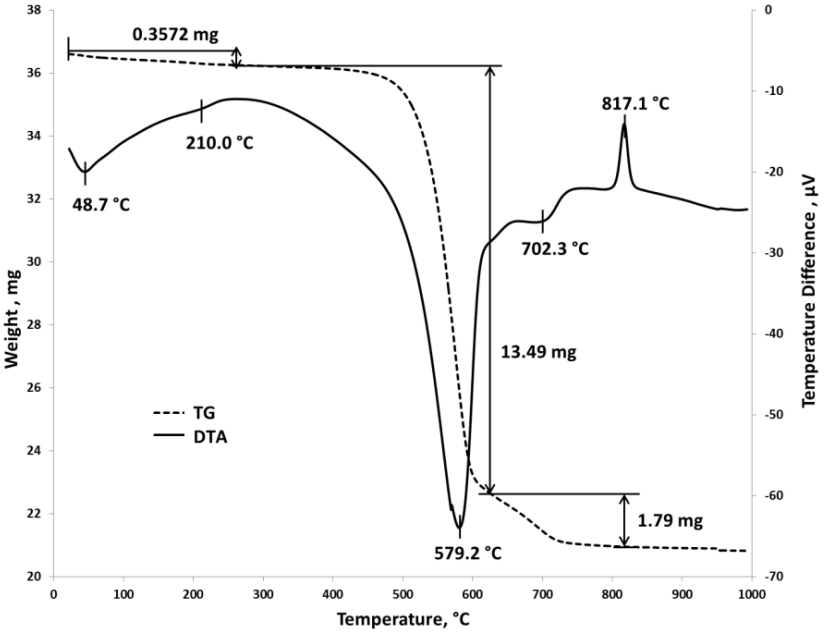

Fig. 2 Thermogram of amorphous magnesite

3.3. *Magnesite*

Thermoanalysis of magnesite sample (fig. 3) shows that decarbonization with formation of magnesium oxide takes place at temperatures of 606.5, 674.8, and 807.2 °C. Also, caustic magnesium oxide which characterized with lower refractive indices, increased unit cell parameters and lower density, is formed in the specified temperature range[5]. It is confirmed with data of determination of specific surface and true density (fig. 5). For example: sample of magnesite burned at temperature range 600-800 °C has the highest specific surface up to 24.1 m^2/g and the lowest true density 2.76 g/cm^3. If temperature increases specific surface abruptly drops, and true density increases with formation of denser MgO particles with more perfect cubic structure of periclase.

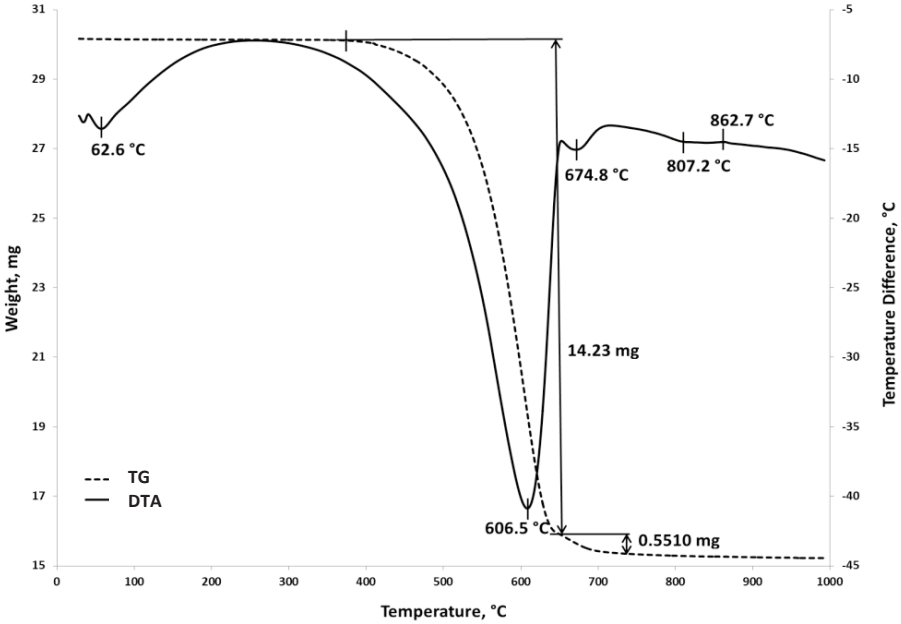

Fig. 3 Thermogram of magnesite

3.4. Hydromagnesite

Thermogram of hydromagnesite sample (fig. 4) shows large amount of various endothermic effects and considerable exothermic effect at temperature of 814.3 °C, which corresponds to appearance of forsterite phase from clinochrysotile. Considerable mass losses and endothermic effect at temperatures of 220-320 °C, corresponding them, is caused by loss of crystallization water from magnesium hydrocarbonate. Then, process of spalling of hydroxyl group occurs that corresponds to endothermic effect at 436.3 °C. Decarbonization takes place in the

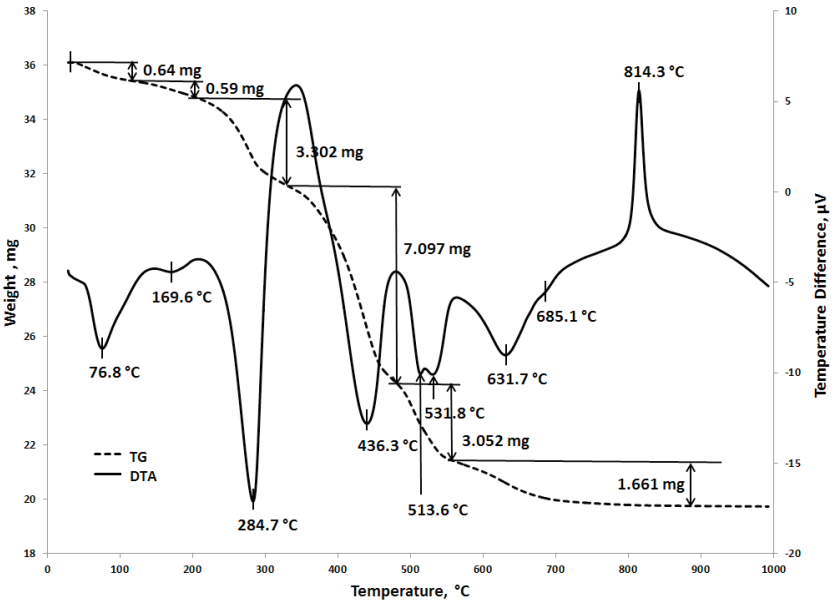

Fig. 4 Thermogram of hydromagnesite

temperature range from 500 to 560 °C. Negligible exothermic effect at 520 °C is connected with partial crystallization of amorphous magnesium carbonate and its following decomposition. Endothermic effects at temperatures of 631.7 and 685.1 °C correspond to processes of decomposition of magnesium carbonate and complete dehydration of clinochrysotile.

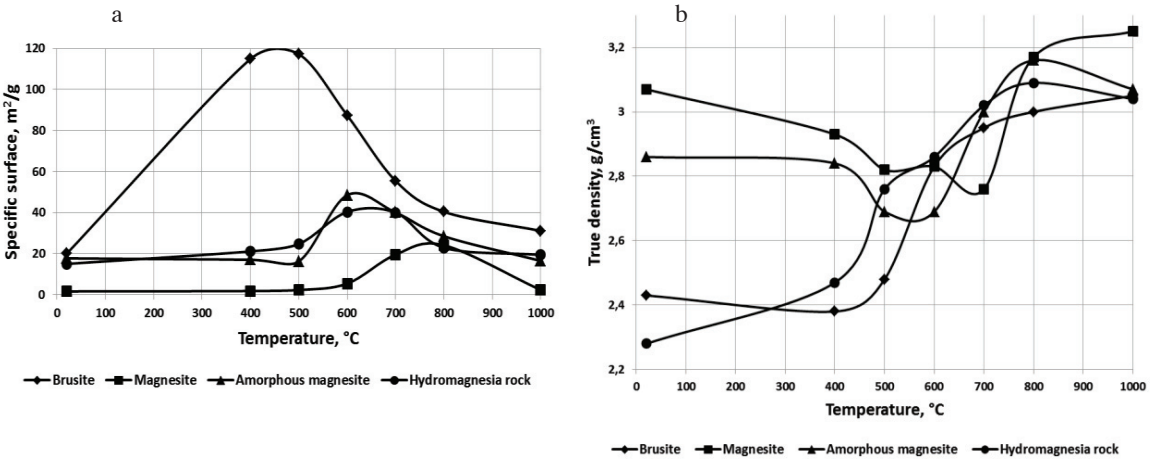

Fig.5 Change of (a) specific surface; (b) of true density of magnesia rock samples at heat treatment

Change of true density of hydromagnesite at ignition has character of gradual increase of values with various intensity. The initial sample has the least value of 2.28 g/cm^3 that corresponds to additive value of density of hydrocarbonate minerals making rocks. Sharp increase of values, caused by processes of dehydration and spalling of hydroxyl group, is observed in the range from 400 to 500 °C. Magnesium carbonates obtained as result of this process form high active magnesium oxide at decarbonization in the time of ignition at the higher temperatures (500-800 °C). Decarbonization process in the temperature range from 500 to 800 °C is accompanying with increase of specific surface values up to 40 m^2/g. With increase of burning temperature the specific surface decreases.

4. Conclusions

Thus, as result of carried out investigations it has been established that to obtain high active magnesium oxide to use it as component of solid phase reactions of synthesis of high refractory materials as the main component of magnesia binder and in other processes and materials it is necessary to perform preliminary burning of magnesia rocks at low or moderate temperatures (500-800 °C). At specified temperatures it is possible to obtain chemical active magnesium oxide with defect crystalline structure and developed surface.

References

1. Sivash V. G., Perepelitsin V. A, and Mitushov N. A. *Fused periclase*. Ekaterinburg: Uralsky rabochiy, 2001 (in Russian)
2. Galimov G. G., Sidorov A. Yu., NikiforovA.A. Investigation of influence of difference of decomposition temperatures of initial compositions down to magnesium and aluminium oxides on intensity of spinel formation reaction (in Russian). *Ogneupory I tekhnicheskaya keramika*. 2014; **9**: 21-26.
3. Zyryanova V. N.,Berdov G. I.. Magnesia binder from refuse of brucite enrichment. (in Russia). *Stroitelnye materialy*. 2006; **4**:61-64.
4. Lotov V. A., and Kutuguin V. A. Technology on the basis of silicate materials of dispersive systems: manual. (In Russian) Tomsk: Publishing Housing of Tomsk Polytechnic university; 2011; 211 p.
5. Zuev V. V., Potselueva L. N., and Goncharova Yu. D. Crystalloenergetics as basis of properties of solid materials (incl. magnesia cements). (In Russian). St- Petersburg, 2006. 139 p.