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Investigations into the kinetics and mechanism of gas–solid state processes in $MgO–MgR_2O_4$ (R: Al, Cr, Fe) spinels–SO_2–O_2 system

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Abstract

In refractory ceramics magnesia-spinel materials continue to play an important role for both economic and research reasons. Although their basic properties are considered to be well-known, problems connected with production technology and improvement of application remain to be solved. The aim of this work is to describe and explain the behaviour of spinels in gaseous environment having high concentration of sulfur oxides.

Thermodynamic analysis of chemical reactions in $MgO–MgR_2O_4$ (R: Al, Cr, Fe) spinels–SO_2–O_2 system as well as kinetic investigations and phase analysis of reaction products were carried out. Kinetic investigation results enabled to compare the chemical reactivity of spinels: $MgAl_2O_4$, $MgCr_2O_4$, $MgFe_2O_4$ and MgO at temperature 773, 1073 and 1273 K. On the basis of shrinking core model activation energy of the reaction $MgO + SO_3 \rightarrow MgSO_4$ was calculated. Kinetic measurements confirmed the influence of early suggested phase changes on chemical reactivity of spinels within characteristic temperature range and revealed unexpectedly high reactivity of $MgFe_2O_4$ in comparison with the other spinels and MgO. It points out the criteria of selecting raw materials in basic refractory ceramics.

Keywords: Kinetics; Topochemical reactions; Spinel; Periclase; Sulfur oxides

1. Introduction

In refractory ceramics magnesia-spinel materials continue to play an important role for both economic and research reasons. Although their basic properties are considered to be well-known, problems connected with production technology and improvement of application remain to be solved. The aim of this work is to describe and explain the behaviour of spinels in gaseous environment having high concentration of sulfur oxides.

Main phases in magnesia-spinel materials are: MgO periclase and MgR_2O_4 type spinels, i.e., $MgAl_2O_4$, $MgCr_2O_4$ and $MgFe_2O_4$.

The application of these materials in copper and cement industry is among others dependent on ensuring their resistance to gas corrosion under the influence of sulfur oxides (SO_2 and SO_3).

Magnesia-spinel materials are characterised by complex phase composition. Apart from pure compounds such as $MgAl_2O_4$, $MgCr_2O_4$ and $MgFe_2O_4$ spinel fraction mostly consists of solid solutions $Mg^{II}(Al,Cr,Fe)^{III}{}_2O_4$—in oxiding atmosphere, or $(Mg,Fe)^{II}(Al,Cr,Fe)^{III}{}_2O_4$—in reducing one.

In the system under consideration, structures of normal spinel ($Mg^{II}Al^{III}{}_2O_4$, $Mg^{II}Cr^{III}{}_2O_4$) [1] as well as inverted spinel ($Fe^{II}(Mg^{II},Fe^{III})_2O_4$) [1–3] may occur. In the spinel structure inversion process is reversible and depends on the rate of system heating or cooling. The phenomenon of spinel inversion may considerably affect the course of chemical reactions in the considered system [4]. On the basis of dilatometric investigations carried out by the authors [4,5] it was found that spinels undergo the process of inversion within the following temperature ranges:

- $MgAl_2O_4$: 903–1073 K in heating cycle and 1093–932 K in cooling cycle.

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- $MgCr_2O_4$: 913–1083 K in heating cycle and 1093–953 K in cooling cycle.
- $MgFe_2O_4$: 763–1083 K in heating cycle.

These results confirm earlier reports on the possibility of phase transitions of the spinel structure related to inversion or space group change [6–10].

The rate of topochemical processes in $MgO–MgR_2O_4$ spinels–SO_2–O_2 system largely depends on the phase composition, texture and size of solid body particles as well as the state of gaseous phase determined by temperature, pressure, composition and flow rate.

To collect thermochemical data for MgO, $MgAl_2O_4$, $MgCr_2O_4$ and $MgFe_2O_4$ spinels, the Chemical Abstracts have been surveyed since 1937. Despite the fact that magnesia-spinel materials are of great practical importance, the literature does not provide data on the kinetics and mechanism of their reaction with sulfur oxides. There are only some kinetic data relating to MgO [11–15] and other pure oxides.

Description of topochemical reaction kinetics always causes a problem and requires knowledge of its mechanism. Although, theoretical models of topochemical reaction kinetics are known, they very often require acceptance of some simplifications of model, which are usually unavoidable due to lack of needed sample parameters: shape of particles, grains size and pore size distribution, diffusion coefficient of gaseous substrate into solid one etc. Those facts prove that this branch of chemistry, i.e., topochemical reaction has not achieved the same degree of theoretical generalisation as chemical reactions in homogenous systems.

Basic model used in the presented paper is SCM (shrinking core model) [20]. In this model the assumption is made that the grains of solid reagent are spherical and the reaction zone shifts towards the center of the grain, thus with the reaction time the radius of unreacted grain decreases. The theory of SCM relate relatively simple, algebraic functions of conversion ratio α_B with the different phenomena, which limiting the reaction rate:

- diffusion resistance in the laminar gas layer,
- diffusion resistance in the layer of solid product,
- resistance of chemical reaction on the phase boundary,
- mixed diffusion-kinetic resistance.

Additionally, different shapes of particles: spheres, plates and cylinders may be also considered in the equation describing SCM.

Models like DPM (distributed pore model) or CGSM (changing grain size model) are special case of SCM including pore size distribution and grain size distribution of solid substrate, respectively. Usually those models fit only special cases and in practice it is difficult to apply them due to lack of the above-mentioned subtle characteristics of powders.

SCM-based models have one essential disadvantage: they do not describe S-shaped conversion time curves, which can be described by PCM (phase change models): Prout-Tompkins' or Avrami's. In PCM a particle first comes to its new temperature where it is unstable and then slowly and isothermally transforms to the product. Prout-Tomkins and Avrami's models differ in their approach to nucleation and growth of product nuclei [20].

Kocaefe et al. [11,12] investigated the rate of reactions of MgO, ZnO and CaO with SO_2 and SO_3 and found that MgO indicated higher reactivity than CaO (at temperature exceeding 900 K). The kinetic models tested by the authors did not precisely describe the results of experiments. Relatively best results were observed for distributed pore model (DPM) [16].

Thibault et al [14] investigated reactivity of MgO and CaO with SO_3, finding analogical kinetic dependences for both oxides. Kinetic curves were described by means of changing grain size model (CGSM) [17].

The detailed objectives of this work are as follows:

(1) To carry out a thermodynamic analysis of chemical reactions in $MgO–MgR_2O_4$ spinels–SO_2–O_2 system and determine the area of particular phases' stability.
(2) To measure the kinetics of reactions of spinels and their mixtures with sulfur oxides at high temperature.
(3) To determine the phase composition of reaction products and explain the mechanism of gaseous corrosion of basic oxides in magnesia-spinel refractory materials.

2. Thermodynamic analysis of chemical reactions in $MgO–MgR_2O_4$ spinels–SO_2–O_2 system

Thermodynamic spontaneity of reactions progressing in the system under consideration was determined on the basis of their standard free enthalpies Δg_j^{Θ} [18], calculated from the following equation:

$$\Delta g_j^{\Theta} = \sum_i \nu_{ij} \Delta G_{fi}^{\Theta} \quad (1)$$

where ν_{ij} are the stoichiometric coefficient of "i" component in "j" reaction, and ΔG_{fi}^{Θ} is the molar free enthalpy of "i" component (kJ/mol).

Sulfates(IV) were neglected in the calculations, as they are unstable at temperature exceeding 700 K.

Calculations were made for the following reactions:

$$MgO + SO_3 \rightarrow MgSO_4 \quad (2)$$

$$MgCr_2O_4 + SO_3 \rightarrow MgSO_4 + Cr_2O_3 \quad (3)$$

$$MgCr_2O_4 + 4SO_3 \rightarrow MgSO_4 + Cr_2(SO_4)_3 \quad (4)$$

$$MgAl_2O_4 + SO_3 \rightarrow MgSO_4 + Al_2O_3 \quad (5)$$

$$MgAl_2O_4 + 4SO_3 \rightarrow MgSO_4 + Al_2(SO_4)_3 \quad (6)$$

$$MgFe_2O_4 + SO_3 \rightarrow MgSO_4 + Fe_2O_3 \quad (7)$$

$$MgFe_2O_4 + 4SO_3 \rightarrow MgSO_4 + Fe_2(SO_4)_3 \quad (8)$$

The results of calculations are given in Fig. 1. Values of Δg_j^{Θ} suggest that within the range of $T < 1200$ K reactions (2)–(8) are thermodynamically spontaneous ($\Delta g_j^{\Theta} < 0$).

Dissociation pressure of sulfates(VI) was calculated using the formulae resulting from the reaction equations.

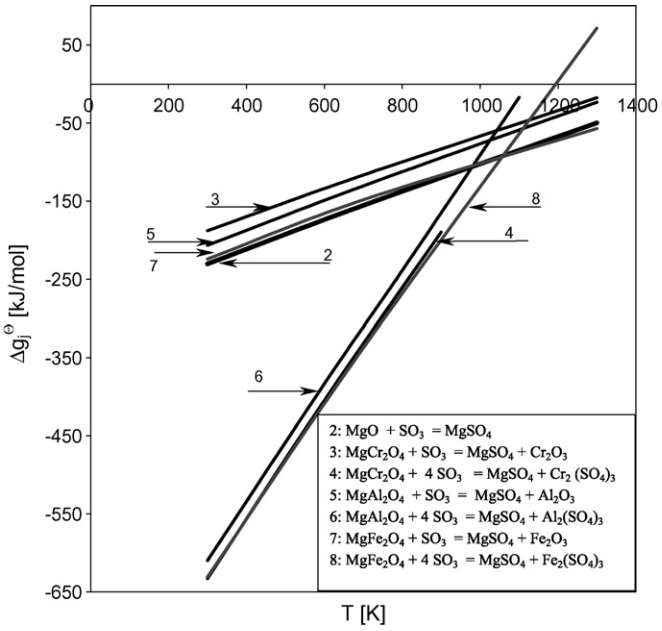

Fig. 1. Standard free enthalpies of reactions (2)–(8) Δg_j^{Θ} (kJ/mol).

For the reaction:

$$MgSO_4 \rightarrow MgO + SO_3 \tag{9}$$

$$\frac{p^*_{SO_3}}{p^{\Theta}} = K_{aj} = \exp\left(\frac{-\Delta g_j^{\Theta}}{RT}\right) \tag{10}$$

where $p^*_{SO_3}$ is the dissociation pressure of sulfate (Pa), p^{Θ} the pressure under standard condition (Pa), K_{aj} the thermodynamic constant of equilibrium, R the gas constant (J/(K mol)) and T is the temperature (K)

For the reactions:

$$Al_2(SO_4)_3 \rightarrow Al_2O_3 + 3SO_3 \tag{11}$$

$$Cr_2(SO_4)_3 \rightarrow Cr_2O_3 + 3SO_3 \tag{12}$$

$$Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + 3SO_3 \tag{13}$$

$$\frac{p^*_{SO_3}}{p^{\Theta}} = K_{aj}^{1/3} = \frac{1}{3}\exp\left(\frac{-\Delta g_j^{\Theta}}{RT}\right) \tag{14}$$

The area of sulfates'(VI) stability is determined by condition: $p^*_{SO_3} < p_{SO_3}$, where p_{SO_3} is a partial pressure of SO_3 in the gaseous phase.

Partial pressure SO_3 in gaseous phase p_{SO_3} was calculated for reaction equilibrium state:

$$2SO_2 + O_2 \leftrightarrow 2SO_3 \tag{15}$$

under conditions: $T = 700$–1500 K, $p = 0.1$ MPa, $x_{0\,SO_2} = 0.12$–0.14, $x_{0\,O_2} = 0.185$. $x_{0\,SO_2}$ and $x_{0\,O_2}$ are the initial mole fraction of substrates, respectively, SO_2 and O_2.

Real partial pressure SO_3 in gaseous phase under conditions of kinetic experiments (for the same composition of gaseous phase) was determined on the basis of chemical analyses of gaseous phase in a reactor and the results of calculations are given in Fig. 2.

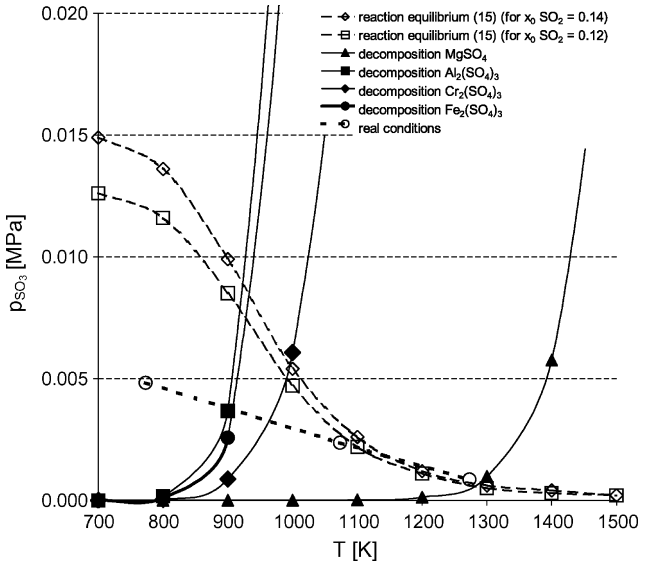

Fig. 2. Dissociation pressure of $MgSO_4$, $Al_2(SO_4)_3$, $Cr_2(SO_4)_3$ and $Fe_2(SO_4)_3$.

Under conditions of kinetic measurements the area of particular sulfates'(VI) stability is as follows:

- $MgSO_4$: $T < 1300$ K.
- $Al_2(SO_4)_3$: $T < 900$ K.
- $Cr_2(SO_4)_3$: $T < 1000$ K.
- $Fe_2(SO_4)_3$: $T < 900$ K.

3. Experimental procedure

$MgAl_2O_4$, $MgCr_2O_4$ and $MgFe_2O_4$ spinels were obtained based on following scheme of chemical reaction:

$$R_2(SO_4)_3{\cdot}nH_2O + MgSO_4{\cdot}7H_2O + 4(NH_4)_2CO_3 = MgR_2O_4{\cdot}nH_2O + 4(NH_4)_2SO_4 + 4CO_2 + 7H_2O \tag{16}$$

where R stands for Al, Fe or Cr.The synthesis of spinels included: preparing the solutions of sulfates(VI) and ammonium carbonate, drying, grinding and calcinations at 1473 K. MgO was obtained by thermal decomposition of $Mg(OH)_2$ at 773 K. Then pellets under 120 MPa pressure were formed and fired at 1923 K for $MgAl_2O_4$, $MgCr_2O_4$ and 1723 K for $MgFe_2O_4$. Pellets were powdered below 0.06 mm [5] in a laboratory ball mill lined with corundum.

Phase composition of the synthesised spinels was verified by XRD diffraction method using PHILIPS diffractometer with Cu X-ray tube and goniometer PW 1050 X' Change, equipped with a graphite monochromator.

Temperature of spinels' inversion was determined by means of SETARAM TMA-92 dilatometer.

Specific surface area of powders was determined by BET method by means of CARLO ERBA SORPTY 1750 device, using nitrogen as adsorbed gas.

Powdered samples' density was determined by pycnometric method.

Bulk density of powders was determined by directly weighing the powder in a platinum boat of known volume.

Table 1
Characteristics of powdered samples

Sample	Specific surface, S_x (m^2/g)	Average grain size (μm)	Density, ρ_0 (kg/m^3)	Bulk density, ρ_n (kg/m^3)	ρ_n/ρ_0
MgO	7.54 ± 0.01	5.0	3549	330[b]	0.09
$MgAl_2O_4$	1.04 ± 0.01	9.0	3550	1070[b]	0.30
$MgCr_2O_4$	0.58 ± 0.01	8.0	4332	1100[b]	0.25
$MgFe_2O_4$	0.16 ± 0.01	10.5	4398	1890[b]	0.43
$MgAl_2O_4/MgCr_2O_4$	Mechanic mixture		3941[a]	1080[b]	0.27
$MgAl_2O_4/MgFe_2O_4$	Mechanic mixture		3974[a]	1370[b]	0.34

[a] Value calculated for samples which are mechanic mixtures.
[b] Average values of measurements performed for samples examined at temperatures of 773, 1073 and 1273 K.

Bulk density ρ_n to density ρ_0 ratio for all tested samples were calculated. The ratio ρ_n/ρ_0 inform about total porosity of the sample according to $(1-(\rho_n/\rho_0))$ 100% dependency. For achieve comparable characteristic of tested samples needed for kinetic investigation, the ratio ρ_n/ρ_0 should be as close as possible for all tested samples.

The following materials were used in kinetic investigations: MgO, $MgAl_2O_4$, $MgCr_2O_4$, $MgFe_2O_4$ spinels as well as mixtures 50/50 wt.% $MgAl_2O_4/MgCr_2O_4$ and 50/50 wt.% $MgAl_2O_4/MgFe_2O_4$.

Kinetic measurements were carried out in the following way: a powdered sample of known mass was put into a platinum boat, and then placed in the tube-type furnace. After the furnace was heated to an adequate temperature (773–1272 K), a process of passing through the system an initially heated gaseous mixture SO_2–air, having the concentration $x_{0\,SO_2} = 0.13$, flow rate 0.03 m^3/h and hold-up time in reactor 130 s was started. Kinetic measurements were carried out at temperature 773, 1073 and 1273 K.

After 1, 2, 4, 6 and 8 h the samples were taken out of the reactor, placed in an exsiccator and weighed after cooling. Weighing of sample as a measure of reaction progress was chosen due to high precision compared to other methods for example quantitative X-ray diffraction analysis, especially in case of low weight changes of the sample. The qualitative X-ray diffraction method for phase composition determination of reaction products was applied.

On the basis of previous measurements [19] and results of thermodynamic analysis it was assumed that reactions (2), (3), (5) and (7) progress in the system. Hence, the conversion ratio (α_B) was calculated for key component—MgO:

$$\alpha_B = \frac{\Delta n_{MgO}}{n_{0\,MgO}} = \frac{M_{MgO}}{M_{SO_3}} \frac{\Delta m_p}{m_{0\,MgO}} \quad (17)$$

where Δn_{MgO} is the change of MgO moles' number, $n_{0\,MgO}$ the initial number of MgO moles, M_{MgO} the molar mass of MgO (g/mol), M_{SO_3} the molar mass of SO_3 (g/mol), Δm_p the sample mass increment and $m_{0\,MgO}$ is the initial mass of MgO in a sample.

4. Results

Basic properties of the samples are presented in Table 1. All the tested spinel powder samples had very close ρ_n/ρ_0 parameters (0.25–0.43), which corresponds to 57–75% total porosity.

The results of product phase analysis (Table 2) fully confirm the course of chemical reactions according to Eqs. (2), (3), (5) and (7). The products contain: $MgSO_4$ as well as free R_2O_3 (R: Al, Cr, Fe) oxides released as a result of spinels' decomposition,

Table 2
Results of phase identification of reaction products (XRD) after reaction with SO_2/SO_3 at temperature 773, 1073 and 1273 K

Sample	Temperature		
	773 K	1073 K	1273 K
MgO	MgO, β-$MgSO_4$	MgO, β-$MgSO_4$	MgO, β-$MgSO_4$
$MgAl_2O_4$	$MgAl_2O_4$, β-$MgSO_4$, α-Al_2O_3, γ-Al_2O_3 in solution with $MgAl_2O_4$	$MgAl_2O_4$, β-$MgSO_4$, α-Al_2O_3, γ-Al_2O_3 in solution with $MgAl_2O_4$, δ-Al_2O_3	$MgAl_2O_4$, β-$MgSO_4$, α-Al_2O_3, γ-Al_2O_3 in solution with $MgAl_2O_4$
$MgCr_2O_4$	$MgCr_2O_4$, β-$MgSO_4$, Cr_2O_3	$MgCr_2O_4$, β-$MgSO_4$ traces, Cr_2O_3 traces	$MgCr_2O_4$, β-$MgSO_4$ traces, Cr_2O_3 not detected[a]
$MgFe_2O_4$	$MgFe_2O_4$, β-$MgSO_4$, Fe_2O_3	$MgFe_2O_4$, β-$MgSO_4$, $MgSO_4$, Fe_2O_3	$MgFe_2O_4$, β-$MgSO_4$, $MgSO_4$ traces, Fe_2O_3 traces
$MgAl_2O_4/MgCr_2O_4$	$MgAl_2O_4$, $MgCr_2O_4$, β-$MgSO_4$, α-Al_2O_3, Cr_2O_3	$MgAl_2O_4$, $MgCr_2O_4$, β-$MgSO_4$, α-Al_2O_3, Cr_2O_3 traces	$MgAl_2O_4$, $MgCr_2O_4$, β-$MgSO_4$, α-Al_2O_3 traces
$MgAl_2O_4/MgFe_2O_4$	$MgAl_2O_4$, $MgFe_2O_4$, β-$MgSO_4$, α-Al_2O_3, Fe_2O_3	$MgAl_2O_4$, $MgFe_2O_4$, β-$MgSO_4$, α-Al_2O_3, Fe_2O_3	$MgAl_2O_4$, $MgFe_2O_4$, β-$MgSO_4$, α-Al_2O_3 traces, Fe_2O_3 traces

[a] Due to low detection threshold in XRD method.

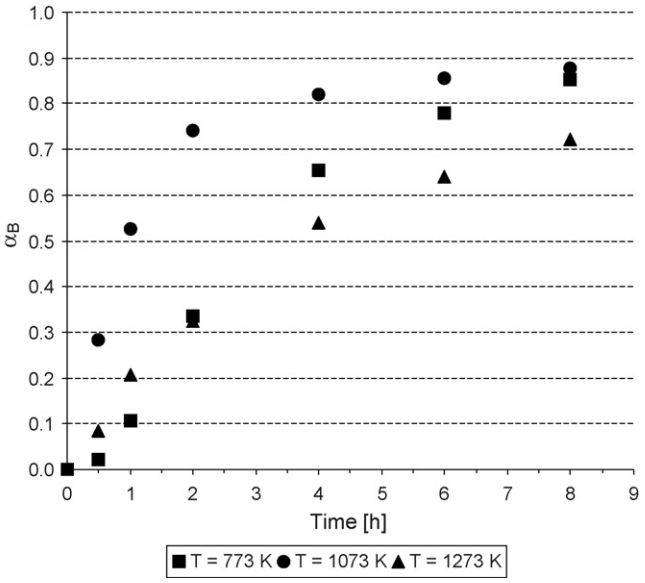

Fig. 3. Conversion ratio (α_B) vs. time. Reaction: $MgO + SO_3 = MgSO_4$.

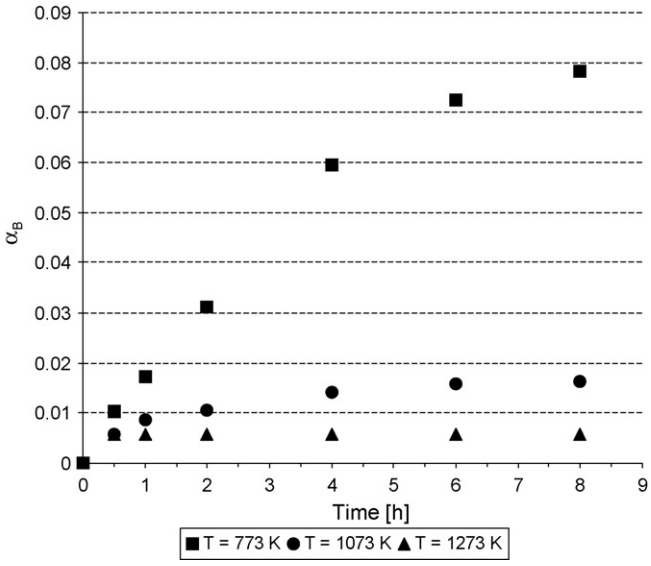

Fig. 5. Conversion ratio (α_B) vs. time. Reaction: $MgCr_2O_4 + SO_3 = MgSO_4 + -Cr_2O_3$.

which is consistent with the results of thermodynamic calculations (Fig. 2). The only exception is the result of phase analysis of the reaction product at temperature 1273 K in case of $MgCr_2O_4$: free Cr_2O_3 was not detected, but also another product β-$MgSO_4$ was detected in very small amounts (traces). It results from generally very low reactivity of $MgCr_2O_4$ at that temperature and does not prove the absence of Cr_2O_3 as a product, which quantity was below detection threshold of XRD method.

The kinetic curves α_B versus time (Figs. 3–8) have a monotonous course, without point of inflexion. For periclase (MgO, Fig. 3) the highest value of α_B was obtained at 1073 K, especially for reaction time shorter than 6 h.

The most intensive reaction of $MgAl_2O_4$ (Fig. 4) was observed at 1073 K.

In case of $MgCr_2O_4$ (Fig. 5) temperature of maximum reactivity was 773 K.

Reactivity of $MgFe_2O_4$ (Fig. 6) was almost the same at temperature 1073 and 773 K up to reaction time 4 h, above this value spinel was more reactive at 1073 K.

Data concerning the reactivity of the mixtures $MgAl_2O_4$/$MgCr_2O_4$ (Fig. 7) and $MgAl_2O_4$/$MgFe_2O_4$ (Fig. 8) seem to confirm behaviour of the separate spinels.

Fraction α_B/S_x, i.e., conversion ratio related to the specific surface area unit S_x, is treated as a measure of reactivity of solid, independent on specific surface area. Relationship α_B/S_x versus time at 1073 K is showed in Fig. 9. Dependence of α_B/S_x versus time at 1073 K may suggest, that at this temperature spinel $MgFe_2O_4$ is even more reactive than free periclase, what is rather unexpected conclusion.

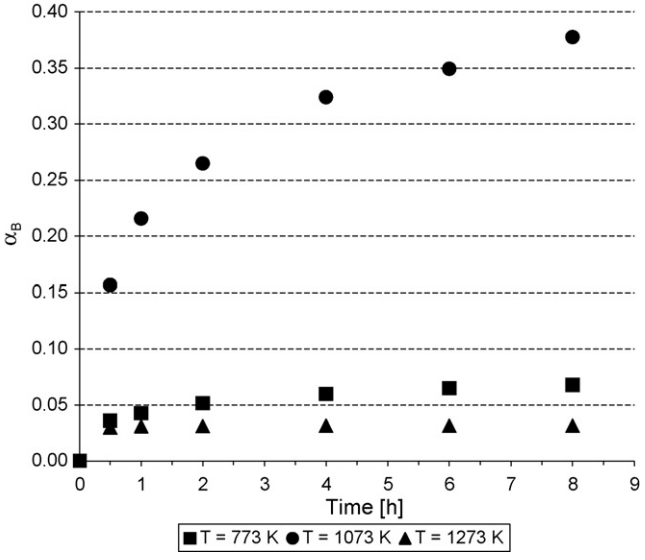

Fig. 4. Conversion ratio (α_B) vs. time. Reaction: $MgAl_2O_4 + SO_3 = MgSO_4 + Al_2O_3$.

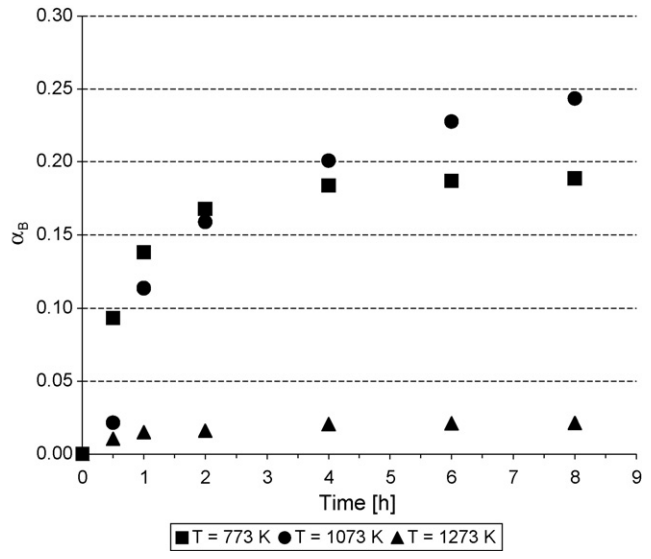

Fig. 6. Conversion ratio (α_B) vs. time. Reaction: $MgFe_2O_4 + SO_3 = MgSO_4 + -Fe_2O_3$.

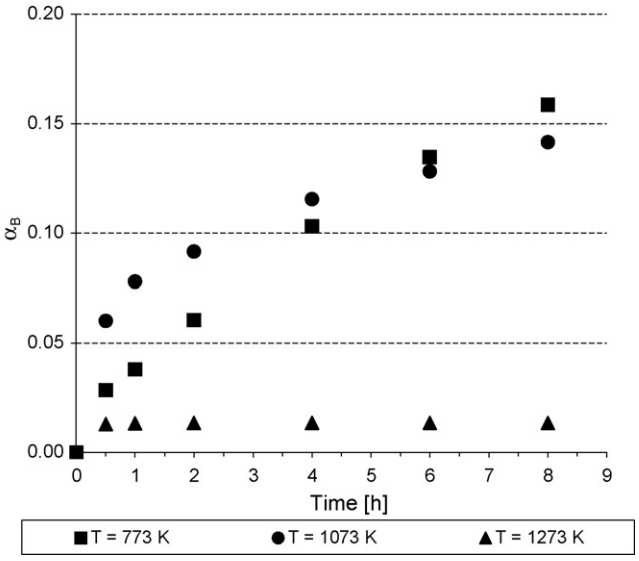

Fig. 7. Conversion ratio (α_B) vs. time. Powder mixture $MgAl_2O_4/MgCr_2O_4$. Reaction: $MgCr_2O_4 + SO_3 = MgSO_4 + Cr_2O_3$ and $MgAl_2O_4 + SO_3 = MgSO_4 + Al_2O_3$.

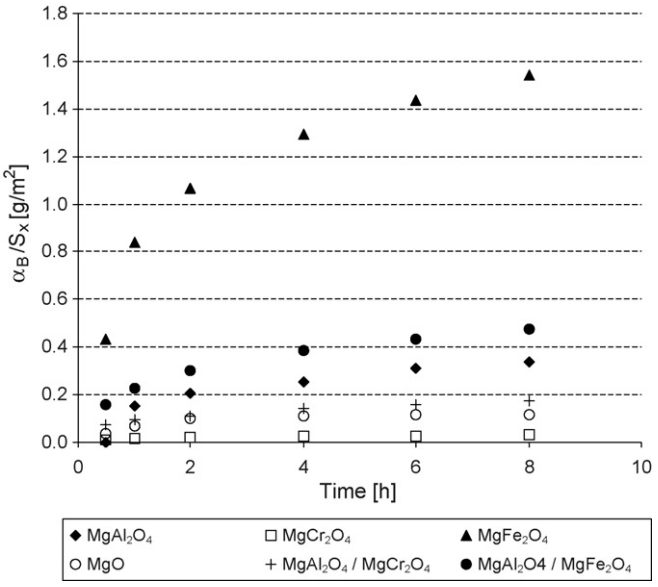

Fig. 9. Conversion ratio (α_B) per specific surface unit α_B/S_x at 1073 K.

5. Discussion

For solid gas chemical reactions several models were worked out, which main feature is connection of measured conversion ratio α_B and time.

To adjust an adequate kinetic equation to the experimental data, calculations were made for five models: two phase change models (PCM) of Prout-Tompkins and Avrami [20] and three based on shrinking core model (SCM) [20] for three different limiting resistances, from which the best correlation for the experimental data was obtained for a SCM of spherical particles and diffusive resistance in product layer. This model corresponds to the following equation:

$$1 - 3(1 - \alpha_B)^{2/3} + 2(1 - \alpha_B) = k_2 t \tag{18}$$

where α_B is the conversion ratio, k_2 the reaction rate constant and t is the time

Assuming that $k_2 = k_2' p_{SO_3}$ and taking the values of partial pressure of SO_3 from Fig. 2 it is possible to calculate k_2'. Such calculations were made for three spinels $MgAl_2O_4$, $MgCr_2O_4$, $MgFe_2O_4$ and MgO, and the dependence $\ln k_2' = f(1/T)$ for every substrate were constructed. Only in case of MgO this relationship was linear (Fig. 10), according to Arrhenius equation:

$$\ln k_2' = \frac{-2327}{T} + 5.54 \tag{19}$$

where correlation coefficient $R = 0.996$.

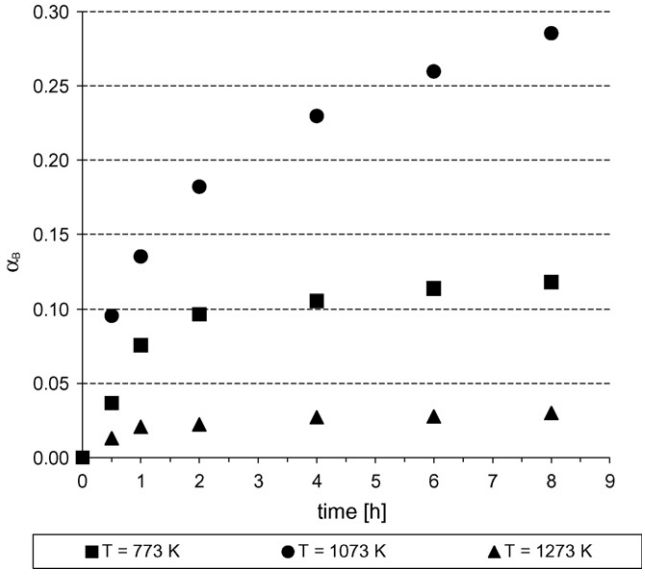

Fig. 8. Conversion ratio (α_B) vs. time. Powder mixture $MgAl_2O_4/MgFe_2O_4$. Reaction $MgAl_2O_4 + SO_3 = MgSO_4 + Al_2O_3$ and $MgFe_2O_4 + SO_3 = MgSO_4 + Fe_2O_3$.

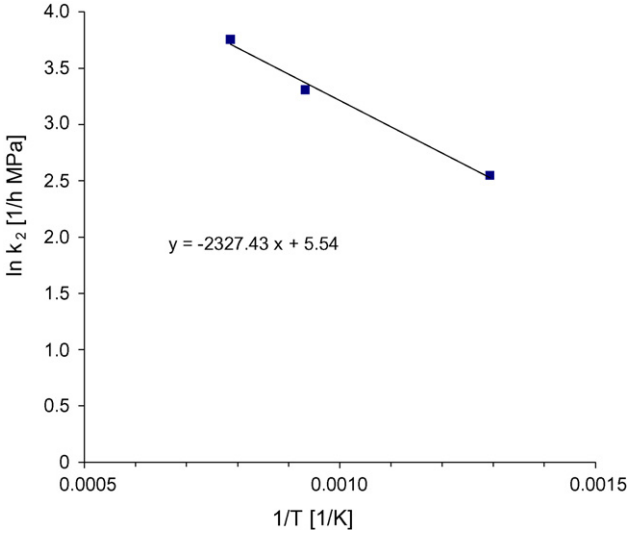

Fig. 10. Reaction rate constant k_2' of MgO vs. temperature.

On this basis activation energy of the reaction MgO and SO_3 was calculated and obtained value $E = 19.35$ kJ/mol fits well the mechanism of diffusion through the product layer.

In case of $MgAl_2O_4$ and $MgFe_2O_4$ dependence of $\ln k_2' = f(1/T)$ was not linear, with maximum at the point corresponding to temperature 1073 K. In case of $MgCr_2O_4$ values of k_2' decrease with temperature.

That proves, those phase changes discussed in introduction really influence reactivity of spinels. Kinetic data make important confirmation of this idea, as maximum reactivity corresponds to the temperature range of structure transformation.

6. Conclusions

Obtained results have practical implication as they enable better understanding of corrosion process of magnesia-chromite and magnesia-spinel refractories.

High reactivity of $MgFe_2O_4$ comparing to other spinels and MgO points out the criterion of selection the proper brands of refractories and the raw materials (chrome ores, co-clinkers) for their manufacturing.

Shrinking core model seems to be appropriate for the purposes of kinetic analysis of MgO, whereas, in case of spinels it should not be applied due to their structural instability within the temperature range of 800–1100 K, confirmed by kinetic data.

From scientific point of view problem of chemical reactivity of spinel solid solutions seems to be very attractive and research in this field should be continued.

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