

The Influence of Order in the Cation Sublattice of MgAl_2O_4 , MgCr_2O_4 and MgFe_2O_4 Spinel on the Kinetics of Topochemical Reactions with Sulphur Oxides

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received September 29, 2016; received in revised form November 21, 2016; accepted February 8, 2017

Abstract

Spinel-containing materials are used as refractories for high-temperature unit linings. A crucial element of the conditions in which they are used is gaseous corrosion caused by sulphur oxides. The aim of the study was to investigate the kinetics of topochemical reactions between magnesia spinels and sulphur oxides and influence of inversion in the structure of the spinels on this reaction. Magnesia spinels: MgAl_2O_4 , MgFe_2O_4 , MgCr_2O_4 were used for the kinetic investigations. It was found that inversion in the case of MgAl_2O_4 begins at approx. 800 K, for MgFe_2O_4 at around 700 K while in the case of MgCr_2O_4 the phenomenon of inversion does not occur. The kinetic measurements were conducted within the temperature range of: 573 – 1073 K for MgAl_2O_4 , 773 – 1073 K for MgCr_2O_4 and 573 – 1173 K for MgFe_2O_4 . The investigations confirmed that the main product of reaction identified in all the cases was MgSO_4 . The inversion of the structure of MgFe_2O_4 and MgAl_2O_4 magnesia spinels was observed to influence the kinetics of their topochemical reactions with sulphur oxides. It is noteworthy that the obtained results indicate that structure inversion has a greater impact on the change of reactivity of MgFe_2O_4 than of MgAl_2O_4 spinel.

Keywords: Order-disorder transformation, spinel, corrosion, refractories, sulphur oxides

I. Introduction

Spinel-containing materials are an important group of refractories used as linings in high-temperature units^{1,2}. An element playing a crucial role in the conditions of their application is gaseous corrosion caused by sulphur oxides: SO_2 and SO_3 . Such corrosion affecting a refractory material that contains spinels is most important in non-ferrous metallurgy, especially in the copper industry, where gaseous corrosion due to reactions between a refractory material and gaseous phase containing SO_2 and SO_3 occurs in the convertor's empty space, over the copper matte^{3–5}. Despite a wide range of applications for spinel-containing materials, the amount of data available on their corrosion caused by sulphur oxides is limited. In works^{6–10} the results of investigations into refractories after service in zones exposed to the corrosive attack of gas containing SO_2 and SO_3 have been presented. However, these investigations did not allow quantitative conclusions to be drawn on the mechanism and kinetics of the corrosion process. This is due to the fact that in real working conditions a refractory material is exposed to the simultaneous effect of many destructive factors. Works^{11,12} present the results of laboratory research on the reactions of basic refractory materials intended for use in copper con-

vertors with a gaseous phase containing oxygen and sulphur dioxide. On the other hand, works^{13–15} present the results of laboratory investigations into the reactions of MgAl_2O_4 , MgCr_2O_4 , MgFe_2O_4 spinels with SO_3 . They revealed that the product of spinel reaction with SO_3 is MgSO_4 , stable at the temperature of 1323 K, as well as free oxides Al_2O_3 , Cr_2O_3 , and Fe_2O_3 ^{13–15}. In works^{11,12} it was found that the products of corrosion of basic refractory materials are MgSO_4 , CaSO_4 , $\text{CaMg}_2(\text{SO}_4)_4$. In investigations^{13,14} into the reactions of magnesia spinels with sulphur oxides it was found that spinel reactivity can be considerably influenced by the order-disorder transformation in the structure of spinel, causing a change of its reactivity in relation to SO_2/SO_3 . This is a second-order transformation accompanied by discontinuity of free enthalpy second derivative, corresponding to such values as: specific heat, thermal expansion coefficient and compressibility factor¹⁶. Inversion of a spinel structure can be induced by temperature and is a reversible phenomenon¹⁷. Spinel structure can change from normal to inverse, which means that divalent ions located in tetrahedral sites swap their positions with trivalent ions and occupy octahedral sites. Spinel structures can be described by the degree of inversion x , which corresponds to the concentration of trivalent cations in the tetrahedral coordination. The degree of inversion x for spinel with a completely normal structure

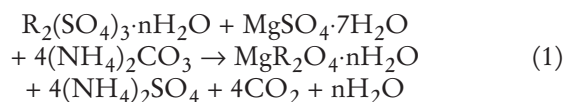
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adopts the value $x = 0$, and for spinel with a completely inverse structure $x = 1$ ^{18–20}. The aim of this work was to examine the kinetics of topochemical reactions of MgAl_2O_4 , MgCr_2O_4 , MgFe_2O_4 spinels with sulphur oxides and determine the influence of the order-disorder transformation (structure inversion) on the kinetics of these reactions.

II. Experimental

(1) Synthesis of one-phase spinels

Spinel precursors were obtained with the method of co-precipitation of sulphates from water solutions, using ammonium carbonate as a precipitating factor. The co-precipitation reaction can be written as the following stoichiometric equation:



where R means Al, Cr, Fe.

To conduct a co-precipitation reaction, equimolar water solutions of sulphates: magnesium and: aluminium, chromium and iron, respectively, were mixed in a 1:1 ratio, then dropped, while still being mixed, into a solution of ammonium carbonate. The amount of precipitating solution was selected such that it contained 100 % excess of ammonium carbonate in relation to the amount resulting from the stoichiometric reaction (1). All the reagents used for synthesis were produced by POCH Gliwice (Poland) and were pure per analysis grade. After the co-precipitation reaction had been completed, the suspension was dried in a sand bath until a solid residue was obtained, which was then ground in an agate mill and calcinated at 1473 K for 4 h in order to remove any ammonium sulphate produced in the precipitation reaction. After calcination, the powders were pressed at 120 MPa and fired in air for 4 h at 1937 K (for MgAl_2O_4 , MgCr_2O_4) and 1723 K (for MgFe_2O_4) because of iron reduction possibility at the higher temperature. The obtained spinels were ground until a grain size smaller than 0.06 mm was obtained.

(2) Methods of spinel research before and after kinetic investigations

Before the kinetic investigations into the reactions of spinels with sulphur oxides were undertaken, the true density (density) and total porosity (porosity) of the spinels were determined by means of an Autopore IV9500 mercury porosimeter produced by Micromeritics; specific surface area was measured with the porosimetric method, using Gemini 2360 equipment produced by Micromeritics, using nitrogen as an adsorbed gas; and bulk density was determined by weighing the powder in a vessel of known volume.

The phase composition was analysed with the X-ray diffraction method, using an X'Pert PRO MPD diffractometer produced by PANalytical, equipped with an X'Celerator detector as well as a graphite monochromator and a lamp with Cu anode. Analyses were carried out for spinels before and after kinetic investigations so as to identify the products of reaction with sulphur oxides. Additionally, the products of reaction were subjected to thermogravimetric analysis, using an STA 409 PC thermal

analyser produced by Netzsch. The analysis was conducted in platinum crucibles with a lid, at a heating rate of 5 K/min and the rate of air flow through the kiln chamber reaching 1.8 dm³/h.

(3) Investigations into the order-disorder transformation in spinels' structure

Three research methods were used to determine the temperature at which the order-disorder transformation begins in the spinels' structure: 1) high-temperature X-ray diffraction – which allows recording of the changes of unit cell parameters and changes of ion positions as temperature increases. For this purpose, the previously mentioned (at point II(2)) X-ray diffractometer, additionally equipped with an Anton Paar HTK 2000 high-temperature oven chamber, was used. During the measurement, the sample was heated at the rate of 5 K/min and measurement data was collected using a different step at various temperature ranges. Up to the temperature of 573 K, the step was 100 K; next, around the inversion temperature, it was 10 K. Before each scan was taken, the sample, having been heated up to the measurement temperature, was thermostated for 10 minutes. Rudiments of the method based on two approaches: 1) determination of the tetra and octahedral site occupancies in the spinel crystal structure and cation - anion distances in tetra and octahedra calculation. Details of the method for determining the degree of inversion have been given in the publication²¹. 2) Dilatometry, which allows recording of the changes in the thermal expansion coefficient as the temperature increases. The temperature of spinel structure inversion was determined with the dilatometric method, by means of DIL 402 C equipment produced by Netzsch. A sample having the dimensions 5 x 5 x 20 mm was heated at the rate of 5 K/min in air atmosphere. 3) Differential scanning calorimetry – which allows the recording of changes in the specific heat as the temperature increases. The temperature of spinel structure inversion initiation was determined with the method of differential scanning calorimetry by means of an STA 409 PC thermal analyser produced by Netzsch. The analysis was conducted in platinum crucibles with a lid, at the heating rate of 20 K/min and the rate of air flowing through the kiln chamber at 1.8 dm³/h. Approximately 145 mg of spinel sample was placed in the crucible.

(4) Kinetic measurements

A scheme of a workstation for kinetic investigations has been presented in work²²; additionally, the reactor was equipped with a system for weighing spinel samples without taking them out of the kiln and interrupting the analysed process. Investigations into spinel corrosive resistance were conducted within the temperature range of 573–1073 K for MgAl_2O_4 , 773–1073 K for MgCr_2O_4 , and 573–1173 K for MgFe_2O_4 . The procedure of kinetic measurements was as follows: a sample of spinel, dried for 1 h at 383 K, was placed in a previously weighed platinum weighing boat. The sample excess was collected by moving a flat plate along the boat walls. This allowed the flatness of the examined sample's surface to be maintained. Everything was weighed on an analytical balance with accuracy

to 0.0001 g. The boat with spinel powder was placed on a platinum sheet, being a part of the weighing system in the kiln. The kiln with the tested sample was heated to the pre-set temperature at the rate of 500 K/h. After reaching the pre-set temperature, the sample was weighed to determine its initial mass (before the reaction). Next, the procedure of pumping a mixture of air and 13 vol% sulphur dioxide into the reactor was started. The intensity of gas flow in the reactor was 69 dm³/h. The current composition of the mixture, depending on temperature, was determined by determining the concentration of SO₂ at the inlet and outlet of the empty reactor, using Reich's iodometric method, which involves chemisorption of SO₂ contained in a particular volume of the analysed gas in a known volume of standard iodine solution. Starch was used as an indicator. Based on the obtained results and the reaction equation $2SO_2 + O_2 = 2SO_3$, the concentration of SO₃ in the reactor was calculated. The spinel sample was weighed after 15 and 30 minutes following the beginning of the reaction and then every 30 min for up to 7 h or until the moment when two subsequent weighings gave the same result. The samples were weighed with accuracy to 0.001 g. Based on previous investigations^{13,14} and precise thermodynamic analysis of the examined system²³, it was found that the following spontaneous chemical reactions were possible:



It was also proved that MgSO₄ is the most thermally resistant product of reaction; under experimental conditions it is stable up to the temperature of 1273 K, whereas Cr₂(SO₄)₃, Fe₂(SO₄)₃, Al₂(SO₄)₃ are stable up to 980 K, 920 K and 910 K, respectively. Based on these findings and the data from earlier works^{13,14}, the manner of calculating the conversion of spinel was adopted according to the following equation:

$$\alpha = \frac{|\Delta n|}{n_0} = \frac{\Delta m}{m_0} \cdot \frac{M_{\text{spinel}}}{M_{SO_3}} \quad (8)$$

where: $|\Delta n|$ – change of the number of spinel moles, n_0 – initial number of spinel moles, Δm – mass change of spinel sample, g, m_0 – initial mass of spinel sample, g, $M_{SO_3} = 80.00$ g/mol, M_{spinel} – spinel molar mass, g/mol. The uncertainty of determining mass change was established to be 0.072 g.

III. Results

The analysis of the phase composition of MgFe₂O₄, MgAl₂O₄, MgCr₂O₄ spinels with the X-ray diffraction method revealed that they were one-phase and did not contain the unreacted starting materials. Table 1 presents the results of determining the specific surface area, porosity, density and bulk density of the spinel powders used for the kinetic investigations.

As indicated by the data presented in Table 1, grains of MgAl₂O₄, MgFe₂O₄, MgCr₂O₄ spinels used for kinetic

investigations were characterized by similar values for specific surface area (0.888, 0.668, and 1.168 m²/g) and similar porosity (56.1, 55.0, 62.9 %). Fig. 1a-c presents the results of determination of the degree of inversion of MgAl₂O₄, MgFe₂O₄, MgCr₂O₄ spinels versus temperature with the X-ray diffraction method.

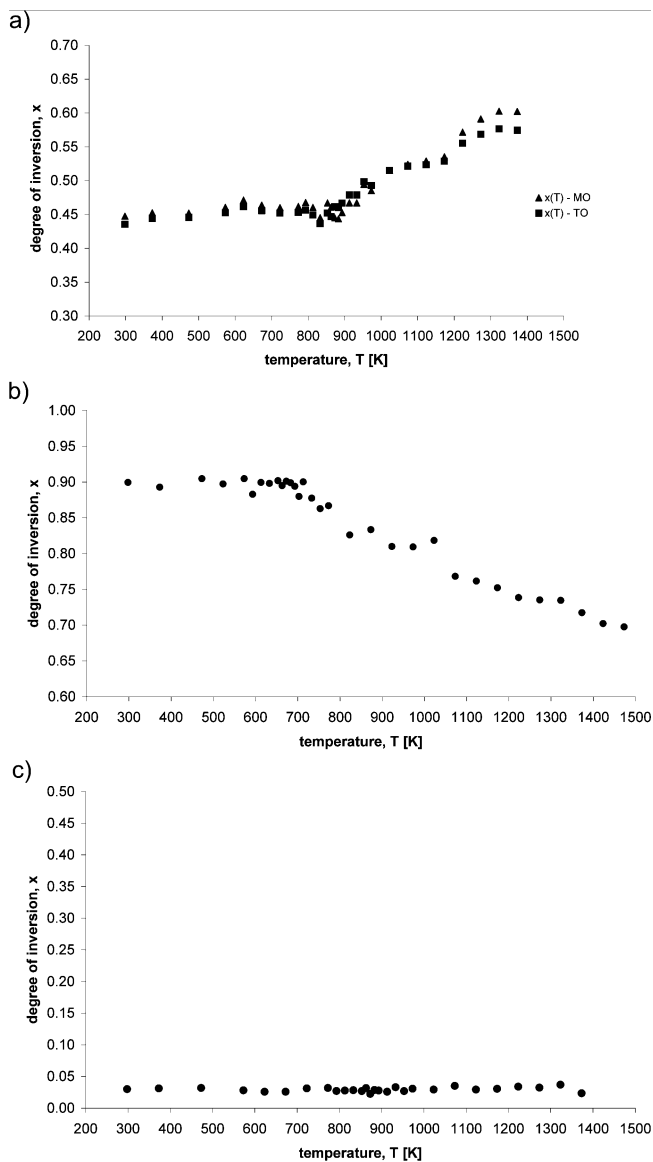


Fig. 1: Degree of spinel inversion x of: a) MgAl₂O₄ – determined from cation-anion bond length in tetrahedral TO and octahedral MO positions, uncertainty of x determination is 0.033, b) MgFe₂O₄, c) MgCr₂O₄ – determined from tetrahedral site occupancy with 3+ cations, uncertainty of x determination is 0.006.

According to literature data^{24,25}, MgAl₂O₄ spinel has a normal-order structure. The order-disorder transformation begins within the temperature range of 933–1223 K and progresses towards the inversion structure. Investigations conducted within the framework of the work revealed that alumina spinel initially has a degree of inversion reaching 0.45. At approx. 800 K the degree of its structure inversion begins to change towards values corresponding to the inversion structure, and at the temperature of 1400 K, it reaches 0.60. It is well known that degree of inversion is dependent on the method of synthesis, for example, in the work of Wood²⁶ the initial degree of inversion

for MgAl_2O_4 obtained with different method and temperature of synthesis was 0.27, 0.39 and 0.37 at 973, 1573 and 1323 K respectively. In the work of Redfern *et al.*²⁷ the initial degree of inversion was 0.14 after sintering at 1773 K. The difference between values of degree of inversion in the samples of the above-mentioned authors and our work was not only temperature but also time of synthesis. Our synthesis was carried out at a higher temperature 1937 K and in a much shorter time, 4 h compared to 42 h²⁷ and 48 h to 9 days depending on the method of synthesis²⁶. It shows that temperature, time and cooling or quenching rate play a key role in the ordering of cations in the spinel structure. The changes in the degree of inversion versus temperature up to 1400 K in the cited references are similar to those in our work and reaches values of approx. 0.15 while the temperature at which order-disorder transformation (inversion) begins is approx. 850 K. Compared to natural spinel, the value of the temperature measured at the beginning of alumina spinel structure inversion is approximately 100 K lower than that quoted in the literature^{28–30}. Natural spinels annealed over geological times also have a lower degree of inversion compared to synthetic ones²⁸.

Table 1: Basic properties of spinel powders used for kinetic investigations.

Spinel	MgAl_2O_4	MgFe_2O_4	MgCr_2O_4
Specific surface area S_x m^2/g	0.888 ± 0.044	0.668 ± 0.033	1.168 ± 0.058
Porosity %	56.1 ± 2.81	55.0 ± 2.75	62.9 ± 3.15
Density g/cm^3	3.501 ± 0.175	4.454 ± 0.223	4.254 ± 0.213
Bulk density g/cm^3	1.43 ± 0.11	1.98 ± 0.18	1.41 ± 0.11

According to literature data²⁴, MgFe_2O_4 spinel has an inverse structure, which is confirmed by research conducted with the method of high-temperature X-ray diffraction, showing that the degree of inversion of the structure of MgFe_2O_4 obtained was 0.90. This means that its structure is very close to the perfectly inverse one. At around the temperature of 700 K, the value of its inversion degree begins to drop and at 1400 K reaches the value of 0.70. As indicated by literature data^{31–33}, the beginning of inversion in the structure of MgFe_2O_4 occurs within the 573–723 K temperature range. The investigations into the degree of inversion of MgCr_2O_4 spinel confirm the literature data²⁴, that is that this spinel has a normal structure and the phenomenon of structure inversion owing to high temperature does not occur in this material. Investigations with the dilatometric method and differential scanning calorimetry also confirmed that inversion of the MgAl_2O_4 structure begins at a temperature higher than 800 K, in the case of MgFe_2O_4 below 700 K, while in MgCr_2O_4 the phenomenon of structure inversion is not observed, as shown in Table 2.

Table 2: Temperature of spinel order-disorder phase transformation beginning determined by: high-temperature X-ray diffraction, dilatometry and differential scanning calorimetry methods.

Method	Temperature of spinel order-disorder phase transformation beginning K		
	MgAl_2O_4	MgFe_2O_4	MgCr_2O_4
High-temperature X-ray diffraction	850	700	-
Dilatometry	> 800	650	-
Differential scanning calorimetry	750–790	670–725	-

Table 3 presents the current composition of gaseous phase in the reactor versus temperature, calculated on the basis of measurements of SO_2 concentration in gas at the inlet and outlet of the reactor. It is noteworthy that as the temperature increases, the content of SO_3 in the gaseous phase drops significantly due to equilibrium SO_2/SO_3 shifts towards SO_2 .

Table 3: Current concentration of SO_3 and conversion of SO_2 in gaseous phase.

Temperature K	Mole fraction and SO_3 partial pressure (at total pressure of 1 bar) $X_{\text{SO}_3}/\text{bar}$	Conversion of SO_2 to SO_3 α
573	0.0705 ± 0.0056	0.532 ± 0.043
673	0.0599 ± 0.0048	0.451 ± 0.036
773	0.0514 ± 0.0041	0.382 ± 0.031
873	0.0449 ± 0.0036	0.338 ± 0.027
973	0.0374 ± 0.0030	0.287 ± 0.023
1073	0.0225 ± 0.0018	0.168 ± 0.013
1173	0.0171 ± 0.0014	0.131 ± 0.010
1273	0.0086 ± 0.0007	0.065 ± 0.005

Figs. 2–4 present kinetic curves of spinel reactions with sulphur oxides in the form of dependence $\alpha = f(t)$ determined from Equation (8) on the basis of mass changes in spinel sample during the kinetic investigations.

Tables 4–6 present the qualitative composition of the reaction products of MgAl_2O_4 , MgCr_2O_4 , MgFe_2O_4 spinels with sulphur oxides established on the basis of investigations with the method of X-ray diffraction and confirmed with thermogravimetry.

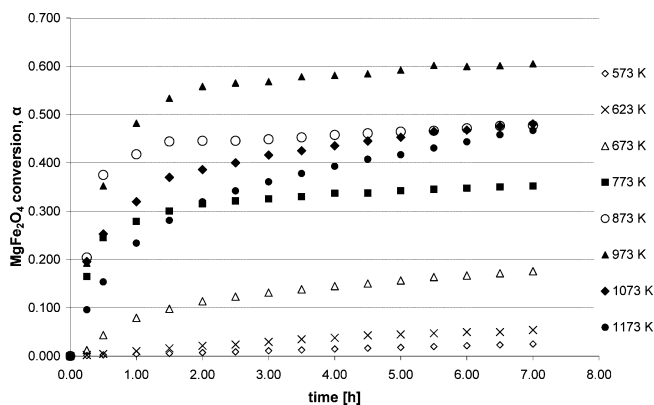


Fig. 2: $MgFe_2O_4$ conversion α versus time and temperature.

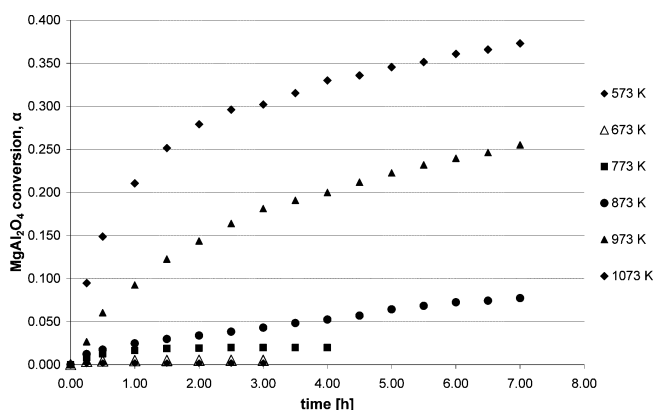


Fig. 3: $MgAl_2O_4$ conversion α versus time and temperature.

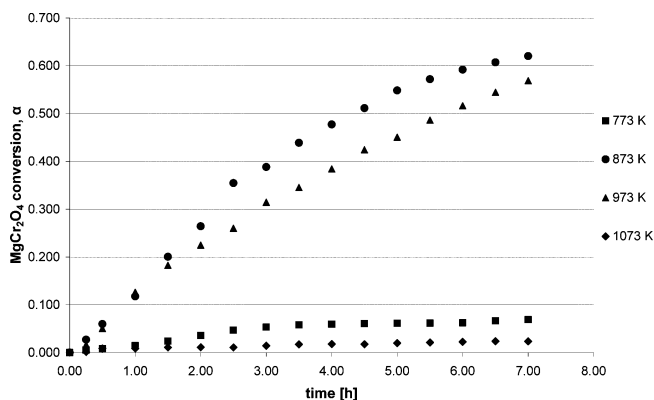


Fig. 4: $MgCr_2O_4$ conversion α versus time and temperature.

Investigations into the products of reaction of magnesia spinels with sulphur oxides revealed that the products of reaction are $MgSO_4$ and a relevant metal oxide R_2O_3 . This indicates that MgO contained in the structure of magnesia spinels is responsible for their reaction with SO_3 . An analysis of spinel samples' phase composition with the method of X-ray diffraction after a reaction at a temperature below 973 K revealed trace amounts of relevant sulphates $R_2(SO_4)_3$ (Tables 4–6). The obtained results are consistent with a thermodynamic analysis of the examined system, indicating that $MgSO_4$ is the most stable among the sulphates produced, whereas the other sulphates $R_2(SO_4)_3$ remain stable up to the temperature of approx. 900 K²³. The composition of the products of reaction also confirms the correctness of the adopted method for calculating the spinel conversion α (Equa-

tion 8); sulphates other than $MgSO_4$ occurred only in trace amounts, which were detected with both the X-ray diffraction method and thermogravimetry.

Table 4: Qualitative composition of $MgFe_2O_4$ spinel samples after a reaction with sulphur oxides (+ means presence of the substance in the sample, – means absence of the substance in the sample).

Temperature K	Phase composition			
	$MgFe_2O_4$	$MgSO_4$	$Fe_2(SO_4)_3$	Fe_2O_3
573	+	+	+	+
623	+	+	+	+
673	+	+	+	+
773	+	+	+	+
873	+	+	+	+
973	+	+	–	+
1073	+	+	–	+
1173	+	+	–	+

Table 5: Qualitative composition of $MgAl_2O_4$ spinel samples after a reaction with sulphur oxides (+ means presence of the substance in the sample, – means absence of the substance in the sample).

Temperature K	Phase composition			
	$MgAl_2O_4$	$MgSO_4$	$Al_2(SO_4)_3$	Al_2O_3
573	+	–	–	–
673	+	–	–	–
773	+	+	–	–
873	+	+	+	–
973	+	+	–	+
1073	+	+	–	+

Table 6: Qualitative phase composition of $MgCr_2O_4$ spinel samples after a reaction with sulphur oxides (+ means presence of the substance in the sample, – means absence of the substance in the sample).

Temperature K	Phase composition			
	$MgCr_2O_4$	$MgSO_4$	$Cr_2(SO_4)_3$	Cr_2O_3
773	+	+	–	+
873	+	+	+	+
973	+	+	–	+
1073	+	+	–	+

IV. Discussion

As the conversion α in topochemical reactions strongly depends on the contact area of gaseous and solid substrates, Figs. 5–8 present dependences between the time and conversion α in relation to the specific surface area S_x of particular spinels.

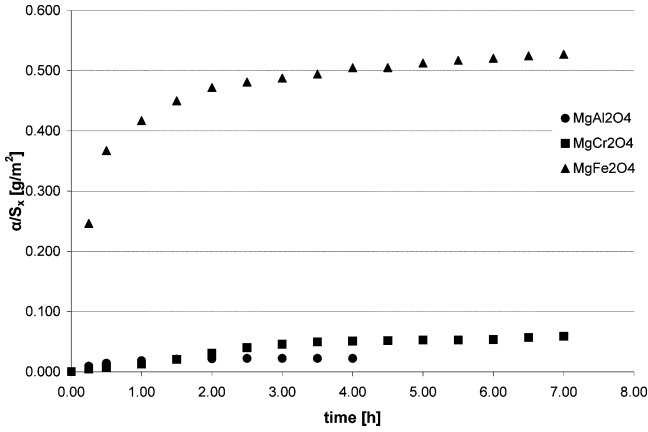


Fig. 5: Conversion α versus time in relation to spinel specific surface area S_x , $T = 773$ K.

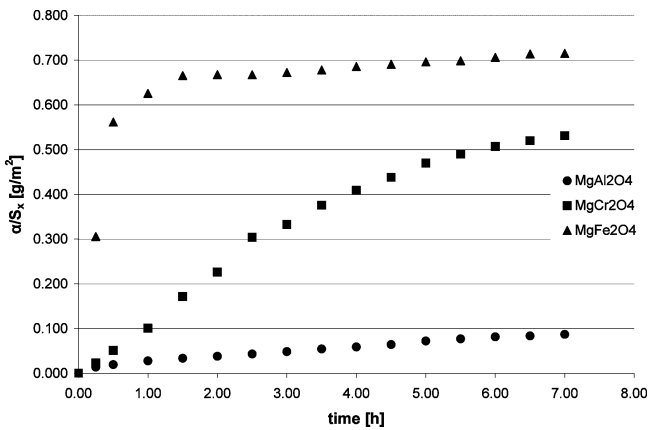


Fig. 6: Conversion α versus time in relation to spinel specific surface area S_x , $T = 873$ K.

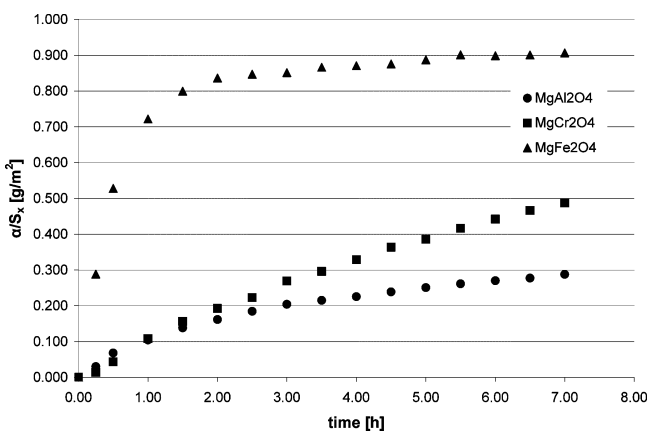


Fig. 7: Conversion α versus time in relation to spinel specific surface S_x , $T = 973$ K.

$MgAl_2O_4$ spinel reaches the maximum conversion $\alpha = 0.373$ at the temperature of 1073 K (Fig. 3), $MgFe_2O_4$ spinel – $\alpha = 0.605$ at 973 K (Fig. 2) and $MgCr_2O_4$ spinel – $\alpha = 0.620$ at 873 K (Fig. 4). After standardization of

the conversion α in relation to the specific surface area S_x (Figs. 5–8) $MgFe_2O_4$ reaches the highest conversion α within the whole temperature range compared to the other two spinels. On the other hand, up to the temperature of 973 K, $MgCr_2O_4$ reaches higher values of the conversion α than $MgAl_2O_4$, whereas at 1073 K it is $MgAl_2O_4$ spinel that is characterized by a higher conversion α .

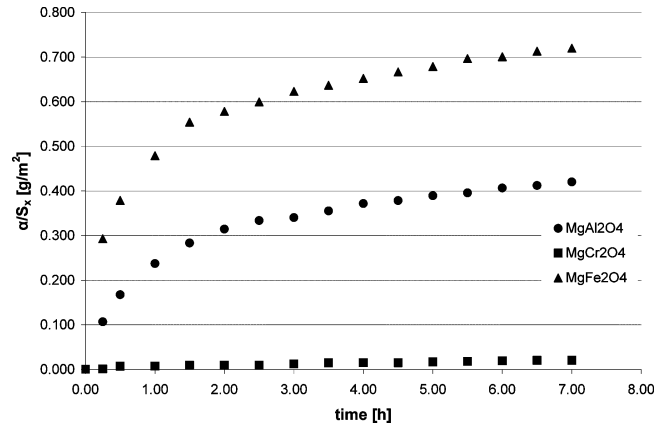


Fig. 8: Conversion α versus time in relation to spinel specific surface area S_x , $T = 1073$ K.

To select a mathematical model describing the kinetic curves obtained, 13 mathematical models were tested. Analysis of the correlation coefficients R^2 indicated that the shrinking core model (SCM) was the most probable. The SCM³⁴ takes into consideration three possible limiting stages: 1) diffusion of a gaseous substrate through a thin layer of gas surrounding the solid substrate, 2) diffusion of a gaseous substrate through the layer of a solid product of reaction, 3) chemical reaction on the phase contact area³⁵ and different shapes of the reacting solid particles of: a sphere³⁵, a cylinder and a plate³⁶. The SCM model for mixed kinetic-diffusion resistance³⁷ was also considered as well as models based on an apparent order of first-, second- and third-order reactions³⁹. Regression analysis was used to determine regression coefficients for the integral form of kinetic equations $f(\alpha) = kt$. The equation fit index for experimental data was assumed to have the value of the correlation coefficient R^2 . The analysis of the correlation coefficients R^2 revealed that experimental data was best described with the SCM model, corresponding to diffusion resistance in the solid product layer for sphere-shaped particles. As shown in Table 7, in the case of $MgAl_2O_4$ this fit is the best at temperatures higher than 873 K, i.e. exceeding the temperature of the order-disorder transformation; for $MgFe_2O_4$ – up to 676 K, i.e. below the transition start temperature; for $MgCr_2O_4$ spinel the fit is good within the whole temperature range subjected to analysis. The integral form of the kinetic equation of the SCM model corresponding to diffusion resistance in the solid product layer for sphere-shaped particles adopts the following form:

$$1 - 3(1-\alpha)^{2/3} + 2(1-\alpha) = kt \tag{9}$$

On the other hand, none of the tested kinetic models describes the experimental data obtained for $MgAl_2O_4$ below the order-disorder transformation start temperature and for $MgFe_2O_4$ above the inversion start temperature.

It is noteworthy that in the case of all the kinetic models subjected to tests, the values of the correlation coefficients adopt similar values: for $MgAl_2O_4$ they are lower at temperatures below the inversion start temperature, while at temperatures above which order-disorder transformation takes place their values increase stepwise. For $MgFe_2O_4$ the case is opposite: below the inversion start temperature the correlation coefficients have higher values, whereas at temperatures exceeding the structure inversion temperature they drop stepwise. On the basis of kinetic Equation (9), the reaction rate constant k was calculated. For a topochemical reaction, the reaction rate constant k not only depends on temperature, but also on the partial pressure of a gaseous substrate, i.e. SO_3 , which results from the kinetic equation of the topochemical reaction³⁹:

$$k(T,p)f(\alpha) = k \cdot pSO_3 \cdot f(\alpha) \quad (10)$$

Table 7: Correlation coefficients R^2 and the reaction rate constants k for Equation (9), SCM model corresponding to diffusion resistance in the solid product layer.

Temperature K	$MgAl_2O_4$		$MgFe_2O_4$		$MgCr_2O_4$	
	R^2	$k \cdot 10^2$ 1/h	R^2	$k \cdot 10^2$ 1/h	R^2	$k \cdot 10^2$ 1/h
573	0.4838	0.000	0.9287	0.003	-	-
623	-	-	0.9786	0.015	-	-
673	0.6073	0.000	0.9783	0.163	-	-
773	0.7588	0.003	0.7215	0.537	0.9374	0.025
873	0.9776	0.030	0.5867	0.964	0.9838	2.960
973	0.9957	0.362	0.7025	2.090	0.9633	2.170
1073	0.9333	0.770	0.8877	1.270	0.9731	0.003
1173	-	-	0.9750	1.320	-	-

Since investigations into the composition of the gaseous mixture in the reactor revealed that the SO_3 concentration considerably dropped with temperature, the value for the real partial pressure of SO_3 in the reactor was taken into account by calculating the value of constant k' in the following way: $k = k' \cdot pSO_3$, i.e. $k' = k/pSO_3$, using constants k' and based on the Arrhenius equation:

$$\ln k' = - E/RT + C \quad (11)$$

where: k' – reaction rate constant taking into account the real concentration of SO_3 in the reactor; E – activation energy, J/mol; $R = 8,314$ J/(mol K) – gas constant; T – temperature, K; C – constant. Activation energies of the reactions of $MgAl_2O_4$ and $MgFe_2O_4$ spinels with SO_3 were determined within the whole analysed temperature range and within a temperature range before and after the beginning of the order-disorder transformation. The obtained values of activation energy are given in Table 8.

Arrhenius curves for $MgFe_2O_4$ and $MgAl_2O_4$ spinels are presented in Fig. 9a and 9b respectively.

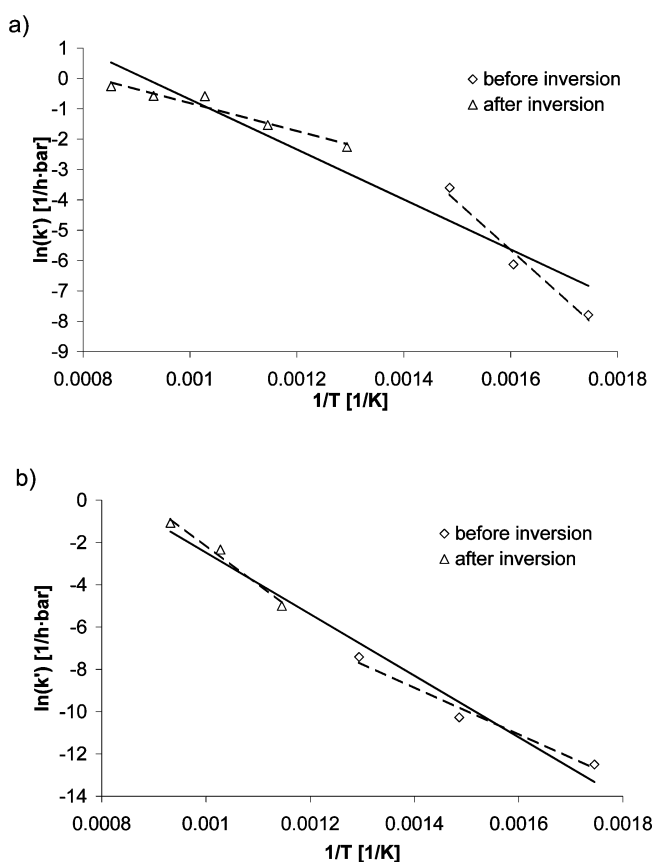


Fig. 9: Arrhenius curves ($\ln k' = f(1/T)$) drawn for the whole investigated temperature range (continuous line) within the temperature range before inversion (rhombuses) and after structure inversion initiation (triangles) for the following spinels: a) $MgFe_2O_4$ and b) $MgAl_2O_4$.

Table 8: Values of activation energy for the reaction of $MgAl_2O_4$ and $MgFe_2O_4$ spinels with SO_3 .

Activation energy E, kJ/mol					
$MgAl_2O_4$			$MgFe_2O_4$		
Whole temperature range 573 – 1073 K	Before inversion 573 – 773 K	After inversion 873 – 1073 K	Whole temperature range 573 – 1173 K	Before inversion 573 – 673 K	After inversion 773 – 1173 K
121.0 ± 9.2	92.3 ± 14.7	154.3 ± 22.4	68.5 ± 7.9	133.3 ± 22.1	38.5 ± 5.5

In the case of the MgCr_2O_4 reaction, the experimental points do not fulfil the Arrhenius equation. The obtained results indicate that structure inversion has a greater impact on a change in the reactivity of MgFe_2O_4 than of MgAl_2O_4 . Degrees of conversion of MgFe_2O_4 below the inversion temperature (measurements at the temperature of 573, 623 and 673 K) are much lower than at temperatures after the initiation of inversion (measurements at 773–1173 K). The rate of reaction (Table 7) of MgFe_2O_4 with SO_3 also increases considerably after the temperature of its structure inversion initiation is exceeded. On the kinetic curves of MgFe_2O_4 (Fig. 2) recorded at temperatures below the inversion start temperature the state of equilibrium $d\alpha/dt \neq 0$ is not achieved, whereas after the temperature of inversion initiation is exceeded the reaction is fast and equilibrium $d\alpha/dt \approx 0$ is achieved. On the Arrhenius plot (Fig. 9a) the straight line going through the measurement points within a temperature range below the inversion start temperature has a different slope than the one within a temperature range above the inversion start temperature; the difference in the reaction activation energy before and after structure inversion initiation is 94.8 kJ/mol. In the case of the MgAl_2O_4 spinel, such a big influence of its structure inversion on reactivity in relation to SO_3 is not observed. The degree of conversion and the rate of MgAl_2O_4 reaction with SO_3 increase considerably only at the temperature of 973 K, i.e. more than 100 K above its structure inversion start temperature. An increase in the degree of conversion and the rate of reaction of MgAl_2O_4 is not so big as in the case of MgFe_2O_4 . On the Arrhenius plot (Fig. 9b) the experimental points for the temperature before and after structure inversion initiation correspond to two straight lines, but the difference in their slope is not as big as for MgFe_2O_4 . The difference in activation energy is 62.0 kJ/mol. The influence of structure inversion on the spinel's reactivity might be proportional to the phenomenon intensity. The degree of MgFe_2O_4 inversion changed by 20 % within the temperature range up to 1400 K (Fig. 1b). The degree of inversion of MgAl_2O_4 within the temperature range up to 1400 K changed by 15 % (Fig. 1a). This might indicate that in MgFe_2O_4 the phenomenon of structure inversion occurs on a larger scale than in the case of MgAl_2O_4 , which translates into its impact on the properties of these spinels and, in consequence, their reactivity in relation to SO_3 . In the spinel crystal structure, 16 from 32 octahedral sites are occupied by cations and only 8 from 64 tetrahedral sites. It is not meaningless which cations occupy particular sites in a crystal structure. These cations that occupied more numerous octahedral sites have the bigger influence on the physical and chemical properties of the spinel. In case of MgAl_2O_4 before the start of order-disorder transformation, Al^{3+} prevailed in octahedral sites ($x = 0.45$) and at high temperature the prevailing cations were Mg^{2+} ($x = 0.60$). In MgFe_2O_4 before the start of order-disorder transformation, more Mg^{2+} cations were located in octahedral sites ($x = 0.90$) and these cations influenced the lower reactivity. After the start of order-disorder transformation, more Fe^{3+} cations moved into octahedral sites ($x = 0.70$) and increased the reactivity of MgFe_2O_4 .

V. Conclusions

Based on the obtained results, it can be concluded that one of the reasons for the wear of basic refractories in the conditions of their exposure to the corrosive effect of sulphur oxides is the phenomenon of gaseous reagents penetrating into the products through open pores and cracks. SO_3 produced in the reaction of SO_2 oxidation reacts with MgO contained in the spinel phase, resulting in the formation of MgSO_4 and free oxides R_2O_3 ($\text{R} = \text{Al}, \text{Fe}, \text{Cr}$), which causes the product's destruction. The formation of MgSO_4 in the cooler zones of a product exerts a stronger influence on its destruction, as MgO in the process of forming MgSO_4 causes a four-fold increase in its molar volume. As a result, the refractory product bursts from the inside, cracks and peels off. Cracks formed owing to corrosion additionally facilitate penetration of a corrosive gaseous medium into the product. The above-described phenomena also lead to an unfavourable change in the phase composition of the refractory product. MgSO_4 , formed at lower temperatures, may decompose when the temperature exceeds the temperature of its thermal decomposition, which, as shown by thermogravimetric investigations into the products of reaction under certain conditions, may start at 1073 K and reach the maximum rate at 1120 K⁴⁰. The difference between the expected decomposition temperature of MgSO_4 (1323 K) and that observed in this work may be explained by the influence of the kinetic factor, e.g. small size of MgSO_4 particles. The temperature gradient in a refractory material, caused by hot zone shifting or by the working cycle (as is the case in heat regenerators), will influence the formation of MgSO_4 , followed by its decomposition, which leads to the formation of reactive MgO . Consequently, instead of a relatively resistant spinel phase, the refractory product contains reactive oxides that are susceptible to chemical corrosion, caused not only by the gaseous phase, but also by slag and metal in contact with the working surface of refractories. The unfavourable phenomenon of corrosion, as shown in the work, may intensify after exceeding the temperature at which inversion of the structure of spinels contained in basic refractory materials is initiated. The conducted investigations reveal the importance of determining which phase component of a refractory material has the lowest corrosive resistance to the attack of a mixture of sulphur oxides and air, as its high content in the material will lead to faster destruction of the refractory product. The results of this work indicate that within the whole temperature range subjected to analysis the highest conversion (after standardization in relation to specific surface area) is observed in the case of MgFe_2O_4 . Since MgFe_2O_4 can be treated as a refractory admixture from resources such as chrome ores and periclase-spinel co-clinkers, it is important to make sure that the content of iron in the raw materials is limited already at the stage of planning the composition of a refractory material to be used as a lining in a zone exposed to attack by sulphur oxides. From the practical point of view, a crucial role in refractory materials is played by MgAl_2O_4 and MgCr_2O_4 spinels; however, it is worth mentioning that due to the pro-ecological trend in the global economy, involving the elimination of chrome compounds, it is

$MgAl_2O_4$ spinel that seems to be gaining importance, as in certain applications it offers an alternative to $MgCr_2O_4$. In the work the authors verified the view that $MgCr_2O_4$ is more resistant to sulphate corrosion than $MgAl_2O_4$. The obtained results indicate that within the temperature range of 773–973 K, $MgAl_2O_4$ spinel achieves lower conversion than $MgCr_2O_4$, whereas at 1073 K the conversion and the rate of $MgAl_2O_4$ reaction are much higher than in the case of the reaction of $MgCr_2O_4$ with SO_3 . This can be explained by the phenomenon of inversion in the structure of $MgAl_2O_4$. Therefore, it can be concluded that at lower temperatures it is alumina spinel that displays much better resistance to corrosion caused by sulphur oxides. On the other hand, at higher temperatures (around 1000 K), when the phenomenon of spinel structure inversion gains importance, the higher reactivity of alumina spinel in relation to sulphur oxides has to be taken into consideration. It should be mentioned that higher reactivity manifests itself in an increase of both the conversion and the rate of reaction. The phenomena of corrosion caused by sulphur oxides and basic refractory materials containing spinels cannot be eliminated, but can be limited. Knowledge of differences in the reactivity of particular phases in the reaction with SO_3 allows the limitation of the content of components that are the most susceptible to the destructive effect of corrosive gaseous phase.

Acknowledgements

The work has been financed by the National Research Centre under the research project number N N209 136840.

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