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Kinetics of the topochemical reaction of the solid solutions of magnesia spinels: $Mg(Cr_{0.5}Fe_{0.5})_2O_4$, $Mg(Al_{0.5}Cr_{0.5})_2O_4$, $Mg(Al_{0.5}Fe_{0.5})_2O_4$ with sulphur oxides

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ABSTRACT

Spinel-containing materials belong to an important group of refractories used as high-temperature unit linings. A crucial element of the conditions in which they are used is gaseous corrosion caused by sulphur oxides: SO_2 and SO_3. In previous investigations into reactions of magnesia spinels with sulphur oxides it was found that spinels' reactivity could be considerably influenced by a phase transition (order – disorder) in the cation sublattice, resulting in a change of their reactivity in relation to SO_2/SO_3.

The aim of the study was to investigate the kinetics of topochemical reactions between equimolar solid solutions of magnesia spinels and sulphur oxides before and after the order – disorder phase transformation in the structure begins. Research into the reaction of equimolar solid solutions $Mg(Cr_{0.5}Fe_{0.5})_2O_4$, $Mg(Al_{0.5}Cr_{0.5})_2O_4$, $Mg(Al_{0.5}Fe_{0.5})_2O_4$ with SO_3 was undertaken due to the fact that spinels form solid solutions in basic refractories. To conduct kinetic measurements, a semi-flow reactor was designed and constructed, in which investigations were carried out at the temperatures of 773 and 973 K and time range: 0–7 h. A mixture of air and SO_2 (13%) was used.

The obtained results have been compared with the kinetic results from the previous work obtained on two-cation spinels: $MgAl_2O_4$, $MgFe_2O_4$, $MgCr_2O_4$. The influence of the degree of inversion in spinel structure on the kinetics of the process was discussed.

1. Introduction

This work concerns the problem of high-temperature sulphate corrosion of basic refractory materials based on magnesium spinels. Spinels are a group of natural and synthetic double oxides with a cubic crystal structure isostructural to $MgAl_2O_4$ [1]. It is known that in the structure of spinel the order-disorder transformation can occur. This is a second-order phase transformation accompanied by the discontinuity of free enthalpy second derivative, corresponding to such values as: specific heat, thermal expansion coefficient and compressibility factor [2]. Inversion of spinel structure can be induced by temperature and is a reversible phenomenon [3,4]. Spinel structure can change from normal to inverse or opposite, which means that divalent cations located in tetrahedral sites swap their positions with trivalent cations and take octahedral sites. Spinel structure 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 adopts the value $x = 0$, and for spinel with a completely inverse structure $x = 1$ [1,5,6]. Investigations [7–10] into the reactions of magnesia spinels with sulphur oxides revealed 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 hypothesis was confirmed in the work [11].

Spinel-containing materials are an important group of refractories used as linings in high-temperature units [12–14]. 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 spinel-containing refractory material is most important in non-ferrous metallurgy, especially 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 gas zone, over the copper matte [15–17]. As spinel forms solid solutions in basic refractories, the aim of this work was to examine the kinetics of the topochemical reaction of

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equimolar spinel solid solutions $Mg(Cr_{0.5}Fe_{0.5})_2O_4$, $Mg(Al_{0.5}Cr_{0.5})_2O_4$, $Mg(Al_{0.5}Fe_{0.5})_2O_4$ with sulphur oxides and compare them with the reaction of two-cation spinels $MgAl_2O_4$, $MgFe_2O_4$, $MgCr_2O_4$ with sulphur oxides.

2. Experimental procedure

2.1. Spinels synthesis

The precursors of $Mg(Cr_{0.5}Fe_{0.5})_2O_4$, $Mg(Al_{0.5}Cr_{0.5})_2O_4$, $Mg(Al_{0.5}Fe_{0.5})_2O_4$, $MgAl_2O_4$, $MgFe_2O_4$, $MgCr_2O_4$ spinels were obtained by 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:

$$R_2(SO_4)_3 \cdot nH_2O + MgSO_4 \cdot 7H_2O + 4(NH_4)_2CO_3 \rightarrow \\ MgR_2O_4 \cdot nH_2O + 4(NH_4)_2CO_3 + 4CO_2 + nH_2O \quad (1)$$

where R means Al, Cr or Fe

To conduct a co-precipitation reaction, equimolar water solutions of: chromium and iron sulphates, aluminium and chromium sulphates, aluminium and iron sulphates, containing 0.25 M of each single sulphate, were mixed in 1:1 vol ratio in the case of spinels solid solutions synthesis. In the case of synthesis of two-cation spinels, a 0.5 M water solution of appropriate sulphate was prepared. Next, an appropriate water solution of aluminium, iron and chromium sulphate or mixed solutions of these sulphates were mixed in the 1:1 vol ratio with 0.5 M solution of magnesium sulphate. The obtained solutions were added, while being stirred, to a 2 M solution of ammonium carbonate. The amount of the precipitating solution was selected in such a way 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 finishing the co-precipitation reaction, the suspension was dried in a sand bath until a solid residue was obtained, which was ground in an agate mill and, next, calcinated at 1473 K for 4 h in order to remove ammonium sulphate produced in the precipitation reaction. After calcination, the powders were pressed at 120 MPa and fired for 4 h at 1937 K in the case of $Mg(Al_{0.5}Cr_{0.5})_2O_4$, $MgAl_2O_4$, $MgCr_2O_4$ and 1723 K in the case of $Mg(Cr_{0.5}Fe_{0.5})_2O_4$, $Mg(Al_{0.5}Fe_{0.5})_2O_4$ and $MgFe_2O_4$ due to the lower melting temperature of these spinels. The obtained spinels were ground until grain size below 0.06 mm was obtained.

2.2. Methods of spinels properties testing

Before undertaking kinetic investigations into the reactions of spinels solid solutions and two- cation spinels with sulphur oxides, their specific surface area was determined by the porosimetric method (using Gemini 2360 equipment produced by Micromeritics, using nitrogen as an adsorbed gas) and bulk density by weighing the powder in a vessel of known volume.

The analysis of phase composition was conducted by the X-ray diffraction method, using an X'Pert PRO MPD diffractometer produced by PANalytical, equipped with an X'Celerator detector and a tube with Cu anode. The temperature at which the order-disorder transition begins in the structure of spinels was determined by the high-temperature X-ray diffraction method, using an Anton Paar HTK 2000 chamber. This method allows recording changes of unit cell parameters, atomic coordination and site occupancies of ions as temperature increases. 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 making each scan, the sample was thermostated for 10 min. The FullProf_Suite software package was applied to determine the oxygen positional parameter u(T), the lattice parameter $a_0(T)$ and the cation site occupancies Occ(T) in each temperature by the Rietveld method. The cation-anion distances in tetrahedral TO(T) and octahedral MO(T) coordination in each temperature were calculated by means of Bond_Str program belonging to the same FullProf_Suite package.

Thus obtained results were used to calculate the degree of inversion in the structure of investigated spinels by means of two methods using various results of calculations.

The first method involved determining the occupation number of tetra- and octahedral sites in the spinel sublattice by 2^+ and 3^+ cations using the Rietveld method. The degree of inversion (x) was determined by calculating the occupation number of tetrahedral positions by 3^+ cations. This method can only be applied when 2^+ and 3^+ cations occupying particular sites in the sublattice differ considerably in their atomic scattering factors. In this work the condition was fulfilled for $MgFe_2O_4$ and $MgCr_2O_4$.

In the case of $MgAl_2O_4$, $Mg(Cr_{0.5}Fe_{0.5})_2O_4$, $Mg(Al_{0.5}Cr_{0.5})_2O_4$, $Mg(Al_{0.5}Fe_{0.5})_2O_4$ this condition was not met. Both Mg^{2+} and Al^{3+} cations have similar values of atomic scattering factor and for this reason the influence of changes in the occupancy of particular sites in the cation sublattice on the intensity of diffraction lines is not observed.

Second method of degree of inversion determination was based on calculation of changes of cation-anion distance. Calculation are based on assumption that the cation-anion distance changes in particular positions in the sublattice proportionally to the changes of cations concentration in this position.

The details of the method for determining the degree of inversion have been given in the works [18,19].

2.3. Kinetic measurements

A diagram of a measuring system for kinetic investigations has been presented in Fig. 1.

The reactor was equipped with a system for weighing samples without taking them out of the kiln and interrupting the analysed process. Investigations into spinels corrosion resistance were conducted at the temperatures of 773 and 973 K. The kinetic measurement procedure was as follows: a sample of spinels solid solution or two-cation spinel, dried for 1 h at 383 K, was placed in a previously weighed platinum boat. The sample excess was collected by moving a flat plate along the boat walls. This allowed maintaining the flatness of the examined sample's surface. The sample in the boat was weighed on an exterior analytical balance with accuracy to 0.0001 g. The boat with the sample 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 so as 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 dm^3/h. The current composition of the mixture, dependant on temperature, was established by determining the concentration of SO_2 at the inlet and outlet of the reactor, using Reich's iodometric method, which involves chemisorption of SO_2 contained in a particular volume of the analysed gas in a known volume of a 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 SO_3 in the reactor was calculated. The spinel sample was weighed after 15 and 30 min following the beginning of the reaction and, next, every 30 min for up to 7 h. The samples were weighed in the measuring system scales with accuracy to 0.001 g. Based on previous investigations [7–11] and a precise thermodynamic analysis of the examined system [20], it was proved that $MgSO_4$ is the most thermodynamically stable product of reaction; under experimental conditions it is stable up to a temperature of 1273 K, whereas $Cr_2(SO_4)_3$, $Fe_2(SO_4)_3$, $Al_2(SO_4)_3$ are stable up to 980 K, 920 K and 910 K, respectively. Calculations of spinel conversion were based on following

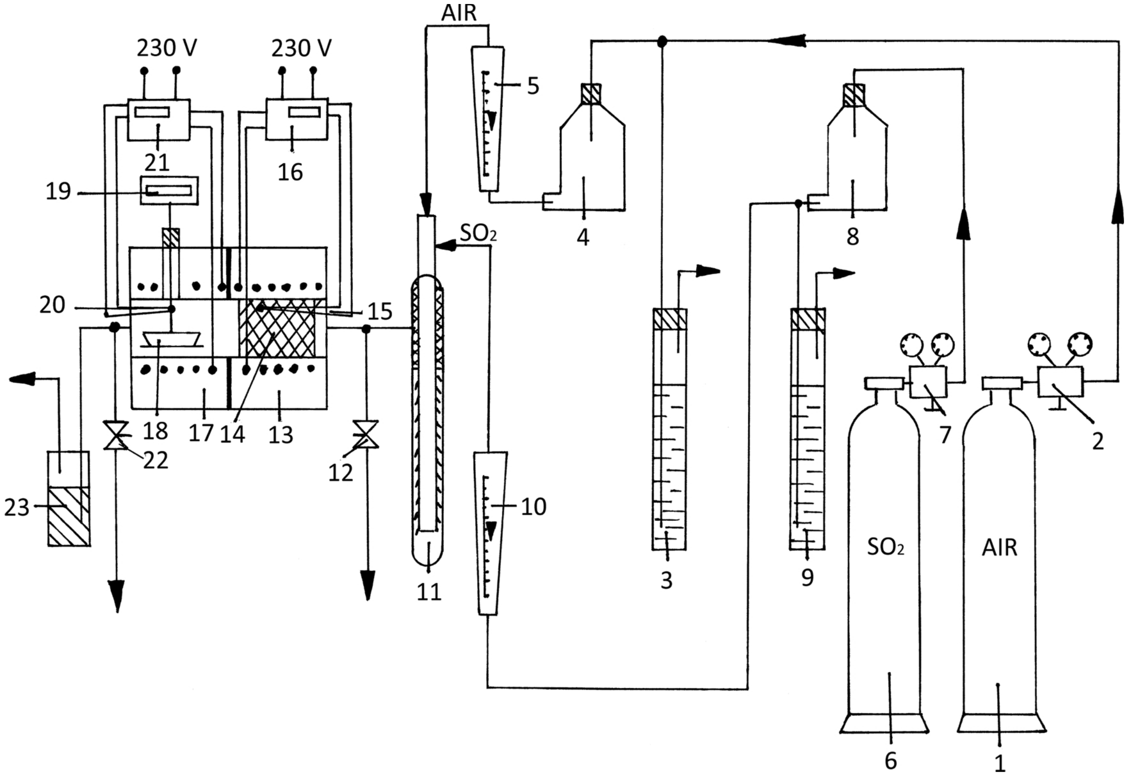

Fig. 1. Diagram of a measuring system for kinetic investigations: 1 – bottle with air, 2 and 7 – reducers, 3 and 9 – manostats, 4 – air dryer, 5 and 10 – rotameters, 6 – bottle with SO_2, 8 – SO_2 buffer tank, 11 – gas mixer, 12 and 22 – gas outlet valves, 13 – gas heater, 14 – heater filling, 15 and 20 – controlling thermocouple, 16 – temperature controller, 17 – furnace (reactor), 18 – sample, 19 – balance, 21 - temperature controller, 23 – washer for collecting oleum.

chemical reactions:

$$2Mg(Cr_{0.5}Fe_{0.5})_2O_4 + 2SO_3 = 2MgSO_4 + Cr_2O_3 + Fe_2O_3 \quad (2)$$

$$2Mg(Al_{0.5}Cr_{0.5})_2O_4 + 2SO_3 = 2MgSO_4 + Al_2O_3 + Cr_2O_3 \quad (3)$$

$$2Mg(Al_{0.5}Fe_{0.5})_2O_4 + 2SO_3 = 2MgSO_4 + Al_2O_3 + Fe_2O_3 \quad (4)$$

$$MgCr_2O_4 + SO_3 = MgSO_4 + Cr_2O_3 \quad (5)$$

$$MgFe_2O_4 + SO_3 = MgSO_4 + Fe_2O_3 \quad (6)$$

$$MgAl_2O_4 + SO_3 = MgSO_4 + Al_2O_3 \quad (7)$$

Calculations of spinel conversion are described by Eq. (8):

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

where: $|\Delta n|$ – change of the number of spinel moles, n_0 – initial number of spinel moles, Δm – sample mass change, g, m_0 – initial sample mass, g, M_{SO3} = 8000 g/mol, M_S – spinel molar mass, g/mol.

The uncertainty of determining the mass change was established to be 0.07 g.

3. Results and discussion

The X-ray diffraction method analysis of the phase composition of solid solutions: $Mg(Cr_{0.5}Fe_{0.5})_2O_4$, $Mg(Al_{0.5}Cr_{0.5})_2O_4$, $Mg(Al_{0.5}Fe_{0.5})_2O_4$ and two-cation spinels: $MgCr_2O_4$, $MgFe_2O_4$, $MgAl_2O_4$ revealed that samples were monophase and did not contain the unreacted starting materials. In Figs. 2–4 the X-ray diffraction patterns of the solid solutions of magnesia spinels are presented.

Table 1 presents the results of determining the specific surface area and bulk density of the spinels solid solutions and two-cation spinels. These powder samples were used for kinetic investigations.

Data presented in Table 1 indicates that spinels powders used for

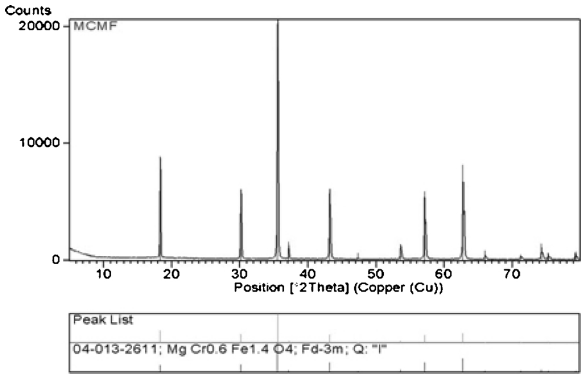

Fig. 2. X-ray diffraction patterns of $Mg(Cr_{0.5}Fe_{0.5})_2O_4$ obtained by the method of co-precipitation of sulphates from water solutions.

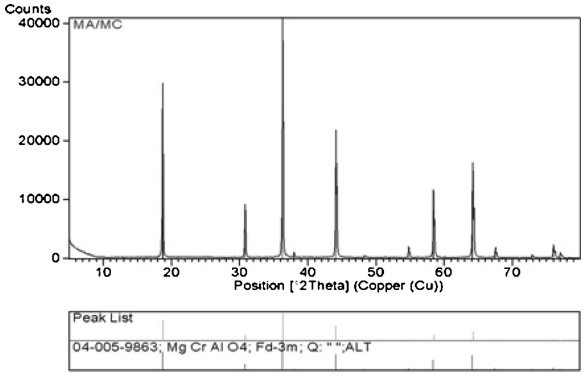

Fig. 3. X-ray diffraction patterns of $Mg(Al_{0.5}Cr_{0.5})_2O_4$ obtained by the method of co-precipitation of sulphates from water solutions.

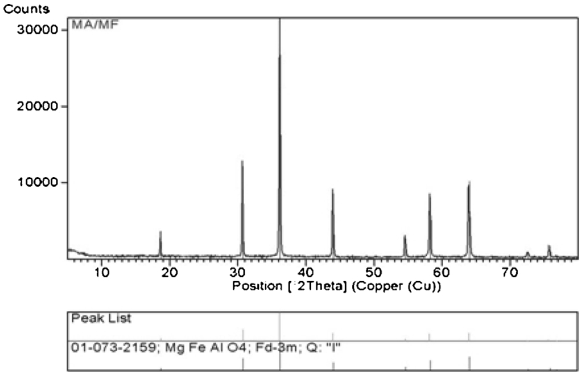

Fig. 4. X-ray diffraction patterns of $Mg(Al_{0.5}Fe_{0.5})_2O_4$ obtained by the method of co-precipitation of sulphates from water solutions.

Table 1
Specific surface area and bulk density of spinels.

Spinel	Specific surface area (S_x m^2/g)	Bulk density (g/cm^3)
$Mg(Cr_{0.5}Fe_{0.5})_2O_4$	0.668 ± 0.033	1.94 ± 0.14
$Mg(Al_{0.5}Cr_{0.5})_2O_4$	0.797 ± 0.040	1.77 ± 0.13
$Mg(Al_{0.5}Fe_{0.5})_2O_4$	0.414 ± 0.021	2.07 ± 0.14
$MgCr_2O_4$	1.168 ± 0,058	1.41 ± 0.11
$MgFe_2O_4$	0.668 ± 0.033	1.98 ± 0.18
$MgAl_2O_4$	0.888 ± 0.044	1.43 ± 0.11

kinetic investigations were characterized by similar values of specific surface area (the smallest one 0.414 m^2/g for $Mg(Al_{0.5}Fe_{0.5})_2O_4$ and the largest one 1.168 m^2/g for $MgCr_2O_4$).

Table 2 presents the results of the degree of inversion determined at room temperature (x_0) and at 1373 K (x_{1373}) as well as its changes (Δx) and the temperature of the order-disorder transformation beginning (T_x).

Initially, the $Mg(Cr_{0.5}Fe_{0.5})_2O_4$ solution is characterized by a mixed structure ($x_0 = 0.50$), at a temperature of ca 800 K its structure transforms into a normal one, reaching the value $x_{1373} = 0.45$ at 1373 K. In works [4,19,20] it has been demonstrated that Cr^{3+} cations do not change their position in the process of heating. During the order-disorder transformation Fe^{3+} cations move to octahedral sites, like in $MgFe_2O_4$ spinel. The change in the degree of inversion of $Mg(Cr_{0.5}Fe_{0.5})_2O_4$ ($\Delta x = 0.05$) is much smaller than in the case of monophase $MgFe_2O_4$ spinel ($\Delta x = 0.20$).

Similarly, in the solid solution of $Mg(Al_{0.5}Cr_{0.5})_2O_4$ the change in the degree of inversion (Δx) depends on Al^{3+} cations moving from octahedral to tetrahedral sites, as is the case of $MgAl_2O_4$ spinel, in which the degree of inversion changes at 850 K from $x_0 = 0.45$ to $x_{1373} = 0.60$. The structure of $Mg(Al_{0.5}Cr_{0.5})_2O_4$ solution at room temperature is similar to the normal one ($x_0 = 0.21$) and becomes only slightly transformed into the inverse structure at 1373 K $x_{1373} = 0.23$. This indicates that the presence of Cr^{3+} ions has a stabilizing effect on the normal structure of $Mg(Al_{0.5}Cr_{0.5})_2O_4$ solution.

Table 2
Initial degree of inversion at room temperature x_0, inversion temperature T_x, degree of inversion at 1373 K x_{1373}, and degree of inversion change Δx of spinels.

Spinel	x_0	T_x (K)	X_{1373}	Δx
$Mg(Cr_{0.5}Fe_{0.5})_2O_4$	0.50	790-810	0.45	0.05
$Mg(Al_{0.5}Cr_{0.5})_2O_4$	0.21	970	0.23	0.02
$Mg(Al_{0.5}Fe_{0.5})_2O_4$	0.51	870–910	0.58	0.07
$MgCr_2O_4$	0.03	–	0.03	–
$MgFe_2O_4$	0.90	700	0.70	0.20
$MgAl_2O_4$	0.45	850	0.60	0.15

The $Mg(Al_{0.5}Fe_{0.5})_2O_4$ solution contains normal $MgAl_2O_4$ spinel and $MgFe_2O_4$ inverse spinel; the structure inversion under the influence of temperature takes place in each of these spinels, which causes that the order-disorder transformation in the $Mg(Al_{0.5}Fe_{0.5})_2O_4$ solution occurs in two directions. Al^{3+} cations move to tetrahedral sites, like in $MgAl_2O_4$ spinel, and Fe^{3+} cations – to octahedral sites, as is the case of $MgFe_2O_4$ spinel. Owing to a larger number of Al^{3+} cations in the spinel lattice, the predominant transition is the one from normal to inverse structure [10]. At room temperature the $Mg(Al_{0.5}Fe_{0.5})_2O_4$ solution has a mixed structure ($x_0 = 0.51$), whereas at around 900 K its structure transforms into an inverse one, reaching the value $x_{1373} = 0.58$ at 1373 K.

Table 3 presents the current composition of the gaseous phase in the reactor versus temperature, calculated on the basis of measurements of SO_2 concentration in the 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.

Figs. 5 and 6 present kinetic curves of spinels solid solutions and two-cation spinels in reactions with sulphur oxides. The course of dependence $\alpha = f(t)$ was determined from Eq. (8).

Table 4 presents the phase composition of the product of reaction of spinels solid solutions and two-cation spinels with sulphur oxides.

Investigations into the products of reaction of spinels solid solutions as well as two-cation spinels with sulphur oxides revealed that the products of reaction are $MgSO_4$ and relevant metal oxides 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 $MgFe_2O_4$ spinel sample phase composition by the X-ray diffraction method, after a reaction at a temperature of 773 K revealed trace amounts of $Fe_2(SO_4)_3$ sulphate. The obtained results are consistent with a thermodynamic analysis of the examined system, indicating that $MgSO_4$ is the most stable among the sulphate products, whereas the other sulphates $R_2(SO_4)_3$ remain stable up to the temperature of ca 900 K [20]. The composition of the products of reaction also confirms the correctness of the adopted manner of calculating conversion α (Eq. (8)); sulphates other than $MgSO_4$ occurred only in trace amounts and at lower temperatures.

As conversion α in a topochemical reaction strongly depends on the contact area of gaseous and solid substrates, Figs. 7–13 present dependences between the time and α in relation to the specific surface area S_x. Standardization of α/S_x allowed direct comparison of the obtained results.

The kinetic dependences obtained at a temperature of 773 K should be treated as results obtained before the commencement of the order-disorder transformation in the structure of the examined spinels, whereas the data obtained at 973 K are the results of investigations conducted at the temperature in which the order-disorder transformation has already begun in all spinels subjected to testing.

As shown in Fig. 7, all the solid solutions of: $Mg(Cr_{0.5}Fe_{0.5})_2O_4$, $Mg(Al_{0.5}Cr_{0.5})_2O_4$ and $Mg(Al_{0.5}Fe_{0.5})_2O_4$ reached a higher conversion (α/S_x) at 973 K than at 773 K (before the commencement of the order-disorder transformation). At a temperature of 773 K, after 7 h, similar values of conversion in relation to specific surface area α/Sx were obtained for $Mg(Cr_{0.5}Fe_{0.5})_2O_4$ and $Mg(Al_{0.5}Fe_{0.5})_2O_4$ solutions – 0.32 g/m^2 and 0.31 g/m^2, respectively. In the case of $Mg(Al_{0.5}Cr_{0.5})_2O_4$ solution, conversion in relation to specific surface area α/S_x obtained after 7 h was considerably lower, reaching 0.05 g/m^2. Similarly, the values of conversion in relation to specific surface α/S_x obtained for $Mg(Cr_{0.5}Fe_{0.5})_2O_4$ and $Mg(Al_{0.5}Fe_{0.5})_2O_4$ solutions at a temperature of 973 K, after 7 h, reached 0.77 g/m^2 and 0.78 g/m^2, respectively, and 0.29 g/m^2 for the $Mg(Al_{0.5}Cr_{0.5})_2O_4$ solution.

In the case of both solid solutions containing iron - $Mg(Cr_{0.5}Fe_{0.5})_2O_4$ (Figs. 8 and 9) and $Mg(Al_{0.5}Fe_{0.5})_2O_4$ (Figs. 10 and 11), conversion in relation to specific surface area α/S_x of the solid solution at 773 K is between α/S_x obtained for $MgFe_2O_4$ and $MgCr_2O_4$ or

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

Temperature (K)	Mole fraction and SO_3 partial pressure (at total pressure of 1 bar) (X_{SO3}, bar)	Conversion of SO_2 to SO_3 (A)
773	0.0514 ± 0.0041	0.382 ± 0.031
973	0.0374 ± 0.0030	0.287 ± 0.023

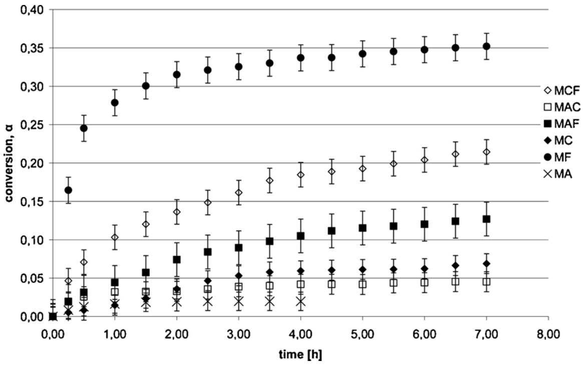

Fig. 5. Conversion α of $Mg(Cr_{0.5}Fe_{0.5})_2O_4$ (MCF), $Mg(Al_{0.5}Cr_{0.5})_2O_4$ (MAC), $Mg(Al_{0.5}Fe_{0.5})_2O_4$ (MAF), $MgCr_2O_4$ (MC), $MgFe_2O_4$ (MF), $MgAl_2O_4$ (MA) versus time at 773 K.

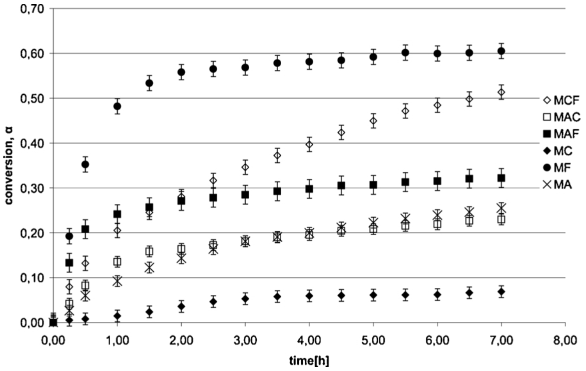

Fig. 6. Conversion α of $Mg(Cr_{0.5}Fe_{0.5})_2O_4$ (MCF), $Mg(Al_{0.5}Cr_{0.5})_2O_4$ (MAC), $Mg(Al_{0.5}Fe_{0.5})_2O_4$ (MAF), $MgCr_2O_4$ (MC), $MgFe_2O_4$ (MF), $MgAl_2O_4$ (MA) versus time at 973 K.

Table 4
Phase composition of spinels solid solutions and two-cation spinels after a reaction with sulphur oxides (+ means presence of the substance in the sample, − means absence of the substance in the sample, R means Al, Cr or Fe).

Spinel	Temperature (K)	Phase composition			
		MgR_2O_4	$MgSO_4$	$R_2(SO_4)_3$	R_2O_3
$Mg(Cr_{0.5}Fe_{0.5})_2O_4$	773	+	+	−	−
	973	+	+	−	+
$Mg(Al_{0.5}Cr_{0.5})_2O_4$	773	+	+	−	−
	973	+	+	−	−
$Mg(Al_{0.5}Fe_{0.5})_2O_4$	773	+	+	−	+
	973	+	+	−	+
$MgCr_2O_4$	773	+	+	−	+
	973	+	+	−	+
$MgFe_2O_4$	773	+	+	+ (traces)	+
	973	+	+	−	+
$MgAl_2O_4$	773	+	+	−	−
	973	+	+	−	+

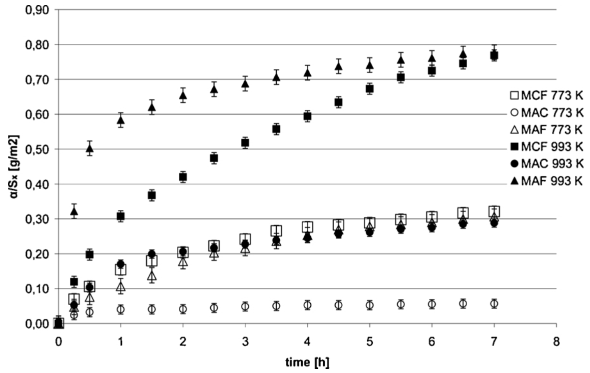

Fig. 7. $Mg(Cr_{0.5}Fe_{0.5})_2O_4$ (MCF), $Mg(Al_{0.5}Cr_{0.5})_2O_4$ (MAC) and $Mg(Al_{0.5}Fe_{0.5})_2O_4$ (MAF), conversion α versus time in relation to spinel specific surface area S_x at the temperatures of 773 K and 973 K.

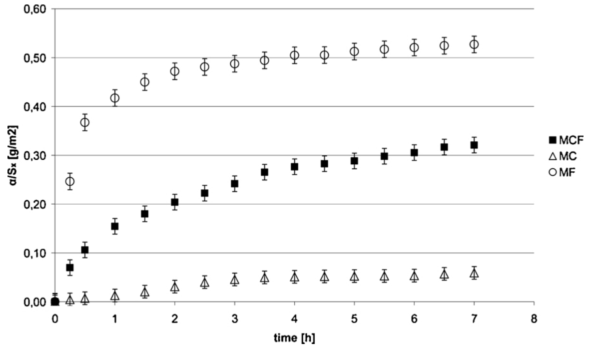

Fig. 8. $Mg(Cr_{0.5}Fe_{0.5})_2O_4$ (MCF), $MgCr_2O_4$ (MC) and $MgFe_2O_4$ (MF) conversion α versus time in relation to spinel specific surface area S_x at a temperature of 773 K.

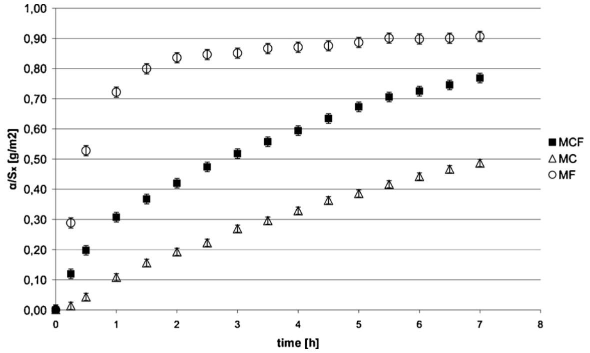

Fig. 9. $Mg(Cr_{0.5}Fe_{0.5})_2O_4$ (MCF), $MgCr_2O_4$ (MC) and $MgFe_2O_4$ (MF) conversion α versus time in relation to spinel specific surface area S_x at a temperature of 973 K.

$MgAl_2O_4$ spinels. At 973 K, conversion in relation to specific surface area α/S_x of the solid solution is close to the value α/S_x of $MgFe_2O_4$ spinel, which contains Fe. It is worth noting that in the case of $Mg(Cr_{0.5}Fe_{0.5})_2O_4$ (Fig. 9) the value of α/S_x is initially closer to the value of α/S_x obtained for $MgCr_2O_4$ spinel, but, with time, it reaches values closer to those obtained for $MgFe_2O_4$. At a temperature of 773 K, when the phenomenon of inversion does not occur in any of the examined spinels, $Mg(Cr_{0.5}Fe_{0.5})_2O_4$ and $Mg(Al_{0.5}Fe_{0.5})_2O_4$ solutions behave like a mixture of particular two-cation spinels. At 973 K - the temperature at

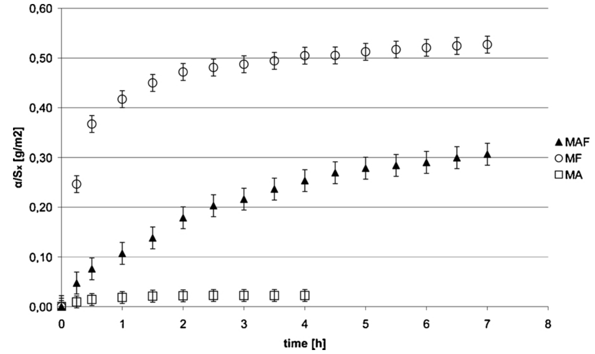

Fig. 10. $Mg(Al_{0.5}Fe_{0.5})_2O_4$ (MAF), $MgFe_2O_4$ (MF) and $MgAl_2O_4$ (MA) conversion α versus time in relation to spinel specific surface area S_x at a temperature of 773 K.

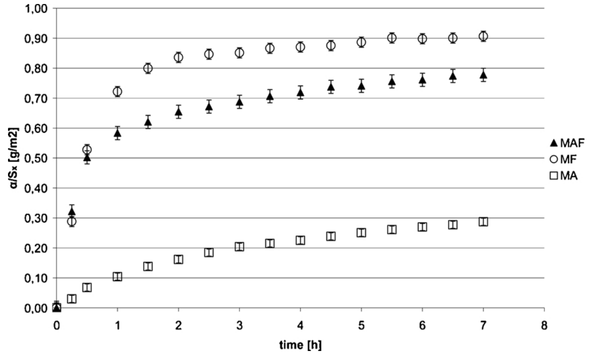

Fig. 11. $Mg(Al_{0.5}Fe_{0.5})_2O_4$ (MAF), $MgFe_2O_4$ (MF) and $MgAl_2O_4$ (MA) conversion α versus time in relation to spinel specific surface area S_x at a temperature of 973 K.

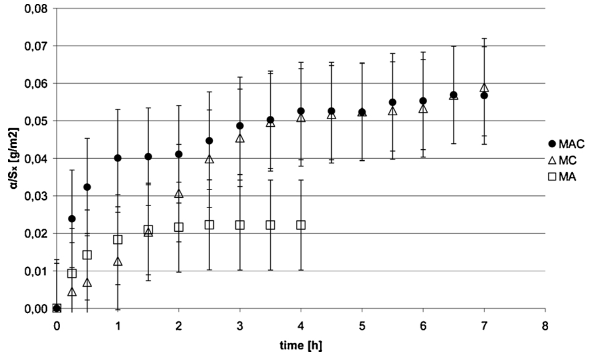

Fig. 12. $Mg(Al_{0.5}Cr_{0.5})_2O_4$ (MAC), $MgCr_2O_4$ (MC) and $MgAl_2O_4$ (MA) conversion α versus time in relation to spinel specific surface area S_x at a temperature of 773 K.

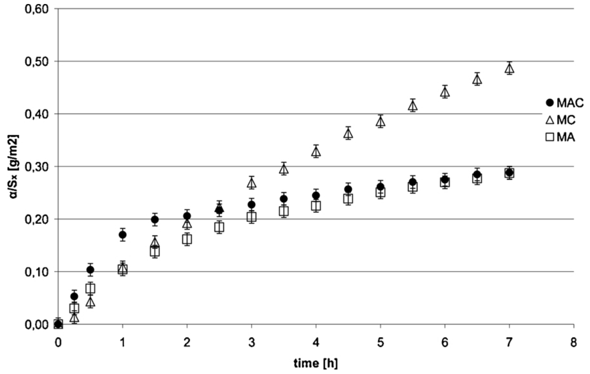

Fig. 13. $Mg(Al_{0.5}Cr_{0.5})_2O_4$ (MAC), $MgCr_2O_4$ (MC) and $MgAl_2O_4$ (MA) conversion α versus time in relation to spinel specific surface area S_x at a temperature of 973 K.

which the order-disorder transformation has begun in both $Mg(Cr_{0.5}Fe_{0.5})_2O_4$ and $Mg(Al_{0.5}Fe_{0.5})_2O_4$ solution, the values of α/S_x are higher than indicated by the average value of α/S_x obtained for respective two-cation spinels.

Investigations into the kinetics of the reactions of two-cation magnesia spinels: $MgAl_2O_4$, $MgFe_2O_4$, $MgCr_2O_4$ with sulphur oxides have demonstrated that the order-disorder transformation in both the structure of $MgAl_2O_4$ and $MgFe_2O_4$ influences the value of the activation energy of these spinels' reaction with sulphur oxides [10,11]. Conversion α determine at temperature before and after order-disorder transformation begins, presented at [10] and the integral form of the kinetic equation of the Shrinking Core Model (SCM) corresponding to diffusion resistance in the solid product layer for sphere-shaped particles:

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

were used to calculate the reaction rate constant k. The SCM model kinetic equation was used because of the best fitting to the experimental data. After including the partial pressure of a gaseous substrate pSO_3 on the reaction rate constant k ($k' = k/pSO_3$) the activation energy E was calculated based on the Arrhenius equation:

$$\ln k' = -E/RT + C \quad (10)$$

where: where: k' – reaction rate constant taking into account the real concentration of SO_3 in the reactor; E – activation energy, J/mol; R = 8314 J/(mol K) – gas constant; T– temperature, K; C– constant.

In the case of $MgAl_2O_4$ spinel, the activation energy of reactions with sulphur oxides at the temperature before the order-disorder transformation begins is 92.3 kJ/mol, and after exceeding the temperature of this transition commencement, it increases to the value of 154.3 kJ/mol. A reverse situation is observed in the case of $MgFe_2O_4$ spinel reaction with sulphur oxides - at the temperature before the order-disorder transformation the activation energy in the spinel structure is 133.3 kJ/mol, whereas after its commencement it drops to the value of 38.5 kJ/mol. Changes in reaction activation energy after exceeding the temperature of the commencement of the order-disorder transformation in the structure of spinels are most probably the reason for an unexpectedly large increase in the value of conversion α/S_x of the solid solutions of spinels containing $MgFe_2O_4$ at a temperature of 973 K.

In the case of $Mg(Al_{0.5}Cr_{0.5})_2O_4$ at a temperature of 773 K (Fig. 12), the solution reacts similarly to $MgCr_2O_4$ spinel. Conversion in relation to specific surface area α/S_x obtained after 7 h for both the $Mg(Al_{0.5}Cr_{0.5})_2O_4$ solution and monophase $MgCr_2O_4$ spinel is 0.06 g/m^2, whereas at 973 K (Fig. 13) the solution of $Mg(Al_{0.5}Cr_{0.5})_2O_4$ reacts like $MgAl_2O_4$ spinel. After 7 h, the value of conversion in relation to specific surface area α/S_x was 0.29 g/m^2 for both samples. Among the examined solutions only in the case of the $Mg(Al_{0.5}Cr_{0.5})_2O_4$ solid solution the values of α/S_x at 773 K were not mean values of α/S_x for respective two-cation spinels, whereas at a temperature of 973 K the values of α/S_x are the same as those observed for the weakest reacting spinel – in this case $MgAl_2O_4$. It is also the only spinel in which the phenomenon of the order-disorder transformation occurring in monophase $MgAl_2O_4$ spinel was practically blocked by the presence of Cr^{3+} cations.

4. Conclusions

Problems encompassed by the conducted investigations are particularly important in copper metallurgy as they are connected with the durability of refractory linings used in this industry. The phenomena of corrosion caused by sulphur oxides cannot be eliminated, but they can be limited. Knowledge about the reactivity of particular phases in relation to sulphur oxides will allow reducing their contents in refractory materials, which are the least resistant to the destructive effect of gases containing sulphur oxides. The results of this work demonstrate that at a temperature of 973 K the presence of Fe in solid solutions of magnesia spinels increases the reactivity of these solutions in relation to sulphur oxides. This is related to the order-disorder transformation in the structure of these solid spinel solutions under the influence of temperature. On the other hand, the reactivity of the solid solution of $Mg(Al_{0.5}Cr_{0.5})_2O_4$ at 973 K is lower than expected – closer to the reactivity of less reactive $MgAl_2O_4$. In this case, the phenomenon of $MgAl_2O_4$ spinel structure stabilization by Cr^{3+} may play an important role.

From the point of view of refractory materials' corrosion caused by sulphates, it seems favourable to reduce the contents of $MgFe_2O_4$ in the composition of refractory materials. Since it can be treated as an admixture from raw materials, such as chrome ores and periclase-spinel co-clinkers, special attention should be paid to a maximum reduction of iron contents in raw materials already at the stage of designing the composition of a refractory material to be used as a lining in the zone exposed to the attack of sulphur oxides.

From the practical point of view, $MgAl_2O_4$ and $MgCr_2O_4$ spinels are the most important in refractory materials. It is worth noting that, due to the pro-ecological trend in global economy, which involves eliminating the use of chromium compounds, $MgAl_2O_4$ spinel becomes particularly important, as it provides an alternative to $MgCr_2O_4$.

However, taking into consideration the obtained results, it seems that elimination of Cr from the composition of a refractory material is unfavourable due to the fact that Cr atoms, which stabilize the structure of $MgAl_2O_4$ spinel, increase its resistance to the effect of sulphur oxides at elevated temperatures.

Acknowledgements

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