Thermochemistry of $MgCr_2O_4$, $MgAl_2O_4$, $MgFe_2O_4$ spinels in $SO_2-O_2-SO_3$ atmosphere☆

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Abstract

The present paper investigates high-temperature sulphate corrosion of basic refractory ceramics containing magnesium spinels ($MgAl_2O_4$, $MgFe_2O_4$, $MgCr_2O_4$ and their solid solutions) widely used in metallurgy, chemical, ceramic and glass industry. This group of refractories are exposed to a number of destructive factors during a working campaign. One of such factors is gas corrosion caused by sulphur oxides. However, gas sulphate corrosion of basic refractory materials containing magnesium spinels, which has a great practical meaning for the corrosion resistance of the material main components, is not sufficiently examined. This work presents a thermodynamic analysis of ($MgCr_2O_4$, $MgAl_2O_4$, $MgFe_2O_4$)$-SO_2-O_2-SO_3$ system aimed to calculate: i) the standard free enthalpy of chemical reactions, ii) the equilibrium composition of the gas mixture initially containing SO_2 and O_2 and iii) sulphates equilibrium dissociation pressure and equilibrium partial pressure for the reaction of SO_3 with the spinels to predict the temperature range of corrosion products' stability. A thermochemical calculation provides information about equilibrium state in the analysed system. In real conditions the state of equilibrium does not have to be achieved. For this reason, the results of calculations were compared with experimental data. The experiment results were consistent with the theoretical predictions.

Keywords: spinels, corrosion, refractories, sulphur oxides

I. 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 the $MgAl_2O_4$ structure as a common feature [1]. Refractories containing magnesium spinels and their solid solutions are widely applied in many branches of industry. When being used, refractory materials are exposed to numerous destructive factors, for example, in glass furnace regenerators, rotary kilns for the production of cement and converter furnaces employed in non-ferrous metals industry. One of such factors is the corrosive effect of gases contain-

ing sulphur oxides. In glass furnace regenerators and rotary kilns for the production of cement the source of sulphur oxides is sulphur-containing fuel. This factor can be eliminated by changing the fuel used to fire the furnace. It is impossible to avoid the emission of sulphur oxides in non-ferrous metals metallurgy, as sulphides are a good source of molten metal. This work has been inspired by the observed process of refractory materials corrosion in the zone over the molten copper matters as a result of sulphur oxides effect [2–4]. The concentration of SO_2 in the converter's gaseous phase ranges between 11 and 14% [5,6]. Literature data confirms that the sulphate corrosion of refractory materials used in converter furnace linings is a major technological problem [7–9]. Investigations into refractories after service in zones exposed to the corrosive effect of gas containing SO_2 and SO_3 have revealed that sulphate corrosion is caused by the formation of $MgSO_4$

[9–11]; however, they have not resulted in quantitative conclusions concerning 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 a simultaneous effect of many destructive factors, such as: chemical reactions, mechanical damage and damage caused by thermal stresses [12,13]. The complexity of the destruction process, which affects refractories working in copper converters, causes the necessity for laboratory tests in which the number of mutually affecting factors is limited. Thus, reactions of basic refractory materials with a gaseous phase containing 80 vol.% of O_2 and 20 vol.% of SO_2 within the temperature range of 973–1623 K have been investigated by Fotoyi *et al.* [14,15]. Three types of commercially available refractory magnesia, chromite-magnesia and magnesia-chromite products have been examined. In the corrosion products the following sulphates have been identified: $MgSO_4$, $CaSO_4$, $CaMg_3(SO_4)_4$ and the most resistant to the attack of sulphur oxides proved to be the magnesia-chromite product. On the other hand, Podwórny *et al.* [16,17] investigated the kinetics of the reactions of MgO and magnesium spinels ($MgAl_2O_4$, $MgCr_2O_4$, $MgFe_2O_4$) with sulphur oxides. The investigations were conducted at a temperature of 773 K, 1073 K and 1273 K in a mixture of air and 13 vol.% of SO_2. It was confirmed that corrosion is caused by the formation of $MgSO_4$ and $MgFe_2O_4$ spinel has higher reactivity in comparison to the other two spinels. Despite the practical meaning of high-temperature sulphate corrosion in the technology of refractories containing magnesium spinels and their solutions, data concerning the corrosive resistance of the product main components is still insufficient. The aim of this work is to better characterize the ($MgCr_2O_4$, $MgAl_2O_4$, $MgFe_2O_4$)–SO_2–O_2–SO_3 system by making thermodynamic calculations and comparing the obtained results with experimental data.

II. Thermodynamic evaluation

The thermodynamic analysis of the ($MgCr_2O_4$, $MgAl_2O_4$, $MgFe_2O_4$)–SO_2–O_2–SO_3 system included: i) calculation of the standard enthalpies Δg_T^Θ of chemical reactions taking place in the system, in order to determine their thermodynamic spontaneity; ii) calculations of the equilibrium composition of a gaseous mixture initially containing 13.0 vol.% of SO_2 and 18.3 vol.% of O_2 within the temperature range of 573–1273 K; iii) calculation of the dissociation pressure of sulphates: $MgSO_4$, $Al_2(SO_4)_3$, $Cr_2(SO_4)_3$, $Fe_2(SO_4)_3$; iv) calculation of equilibrium partial pressure $p_{SO_3}^*$ for the reactions of the spinels ($MgCr_2O_4$, $MgAl_2O_4$, $MgFe_2O_4$) with SO_3.

It was assumed that the independent chemical reactions occur in the examined systems, which have been described by the equations (1–6) given below:

$$MgCr_2O_4 + SO_3 \rightleftharpoons MgSO_4 + Cr_2O_3 \qquad (1)$$

$$MgCr_2O_4 + 4SO_4 \rightleftharpoons MgSO_4 + Cr_2(SO_4)_3 \qquad (2)$$

$$MgAl_2O_4 + SO_3 \rightleftharpoons MgSO + Al_2O_3 \qquad (3)$$

$$MgAl_2O_4 + 4SO_3 \rightleftharpoons MgSO_4 + Al_2(SO_4)_3 \qquad (4)$$

$$MgFe_2O_4 + SO_3 \rightleftharpoons MgSO_4 + Fe_2O_3 \qquad (5)$$

$$MgFe_2O_4 + 4SO_3 \rightleftharpoons MgSO_4 + Fe_2(SO_4)_3 \qquad (6)$$

2.1. Standard free enthalpies

Standard free enthalpies for the reactions 1–6 were calculated according to the equation (7):

$$\Delta g_T^\Theta = \sum \nu_i \Delta G_{fTi}^\Theta \qquad (7)$$

where ν_i is stoichiometric coefficient of component "*i*" and ΔG_{fTi}^Θ is standard free enthalpy of the formation of component "*i*" at a given temperature read out from Barin's tables [18].

2.2. Equilibrium composition of a gaseous phase

Calculations of the equilibrium composition for the reaction $2SO_2 + O_2 \rightleftharpoons 2SO_3$ were conducted by calculating the thermodynamic equilibrium constant of the gaseous reaction:

$$K_{ap} = \exp\left(-\frac{\Delta g^\Theta}{RT}\right) \qquad (8)$$

For the condition $p \approx 1$ bar it can be assumed that reagent pressure activity coefficients $\phi_t \approx 1$, therefore:

$$K_{ap} = K_p = K_x \left(\frac{p}{p^\Theta}\right)^{\Delta\nu} \qquad (9)$$

where p is current pressure in the system, p^Θ is pressure in the standard state ($p^\Theta = 1$ bar) and $\Delta\nu$ is change in the number of mols:

$$\Delta\nu = \sum \nu_i = -1$$

The stoichometric balance results in the following dependences:

$$x_i^* = \frac{x_{0i} + \frac{\nu_i}{|\nu_A|} \cdot x_{0A} \cdot \alpha_A^*}{1 + \frac{\Delta\nu}{|\nu_A|} \cdot x_{0A} \cdot \alpha_A^*} \qquad (10)$$

$$K_x = K_{ap} = \prod x_i^{*\nu_i} = \frac{\prod\left(x_{0i} + \frac{\nu_i}{|\nu_A|} \cdot x_{0A} \cdot \alpha_A^*\right)^{\nu_i}}{\left(1 + \frac{\Delta\nu}{|\nu_A|} \cdot x_{0A} \cdot \alpha_A^*\right)^{\Delta\nu}} \qquad (11)$$

$p = 1$ bar

The solution of equation (11) allows calculating the value of the equilibrium degree of the change of reagent A ($\alpha_A^* = \alpha_{SO_2}^*$). In addition, from equation (10) it is possible to calculate the equilibrium composition of the gaseous phase for the assumed initial concentrations of SO_2, O_2 and temperature.
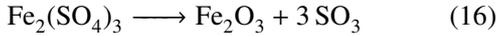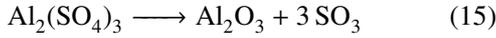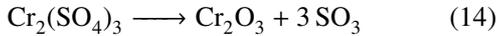
2.3. Dissociation pressure of sulphates

Sulphates, as products in the reactions 1–6, in appropriate thermodynamic conditions will be subject

to thermal decomposition. To determine the conditions in which sulphates $MgSO_4$, $Al_2(SO_4)_3$, $Fe_2(SO_4)_3$, $Cr_2(SO_4)_3$ will be thermodynamically stable or decompose, the value of equilibrium pressure SO_3 (dissociation pressure) $p^*_{SO_3}$ was calculated for each of these reactions. The calculations were based on thermodynamic equilibrium constants of particular sulphates thermal decomposition reactions. Thus, for the reaction of magnesium sulphate decomposition:

$$MgSO_4 \longrightarrow MgO + SO_3 \qquad (12)$$
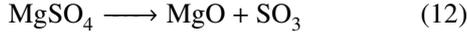
$$K_a = K_{ap} = K_p = \left(\frac{p^*_{SO_3}}{p^\Theta} \right) \qquad (13)$$

For the reaction of chromium, aluminium and iron sulphates:

$$Cr_2(SO_4)_3 \longrightarrow Cr_2O_3 + 3\,SO_3 \qquad (14)$$
$$Al_2(SO_4)_3 \longrightarrow Al_2O_3 + 3\,SO_3 \qquad (15)$$
$$Fe_2(SO_4)_3 \longrightarrow Fe_2O_3 + 3\,SO_3 \qquad (16)$$

$$K_a = K_{ap} = K_p = \left(\frac{p^*_{SO_3}}{p^\Theta} \right)^3 \qquad (17)$$

The values of equilibrium constants K_a were calculated on the basis of equilibrium constants of the reaction of formation K_{fi}:

$$\log K_a = \log K_{ap} = \sum \nu_i \log K_{fi} \quad T = const. \quad (18)$$

K_{fi} values were read out from Barin's tables [18].

2.4. Equilibrium partial pressure for reactions of spinels with SO_3

Equilibrium partial pressures $p^*_{SO_3}$ for the reactions of spinels with SO_3 (equations 1–6) were calculated using the equilibrium constants temperature dependences. For the reactions 1, 3 and 5, the following dependences are fulfilled:

$$K_{ap} = \left(\frac{p^*_{SO_3}}{p^\Theta} \right)^{-1} \qquad (19)$$

$$\ln K_{ap} = -\frac{\Delta g^\Theta}{RT} = -\ln \left(\frac{p^*_{SO_3}}{p^\Theta} \right) \qquad (20)$$

$$\ln \left(\frac{p^*_{SO_3}}{p^\Theta} \right) = \frac{\Delta g^\Theta}{RT} \qquad (21)$$

For the reactions 2, 4 and 6 the following dependences are fulfilled:

$$K_{ap} = \left(\frac{p^*_{SO_3}}{p^\Theta} \right)^{-4} \qquad (22)$$

$$\ln K_{ap} = -\frac{\Delta g^\Theta}{RT} = -4 \ln \left(\frac{p^*_{SO_3}}{p^\Theta} \right) \qquad (23)$$

$$\ln \left(\frac{p^*_{SO_3}}{p^\Theta} \right) = \frac{1}{4} \cdot \frac{\Delta g^\Theta}{RT} \qquad (24)$$

III. Experimental

Corrosive resistance of magnesium spinels and their solid solutions have been investigated to verify the thermodynamic calculations. Tests were done for the single phase spinels ($MgCr_2O_4$, $MgAl_2O_4$, $MgFe_2O_4$) and their equimolar solid solutions ($MgAlCrO_4$, $MgAlFeO_4$, $MgFeCrO_4$) obtained by the co-precipitation method from water solutions. The applied reagents were p.a. grade produced by POCH (Gliwice, Poland). From pure Mg, Al, Fe and Cr sulphates the water solutions with appropriate ionic concentration were prepared and added drop wise in continuously stirred precipitating agent (ammonium carbonate water solution). The slurry was dried and calcinated at 1473 K and the obtained spinel precursors were fired at 1937 K (spinels without iron) and 1732 K (spinels containing iron). The fired samples were ground to a grain size less than 0.06 mm.

The phase composition of the obtained spinels and their solid solutions as well as the composition of the products of reaction with the gaseous phase containing sulphur oxides were identified by the X-ray diffraction method, using an X'Pert PRO MPD diffractometer produced by PANanalytical, equipped with an X'Celerator RTMS detector as well as a graphite monochromator and a lamp equipped with a Cu anode. Investigations into spinel corrosion resistance were conducted within a temperature range of 573–1073 K for $MgAl_2O_4$, 773–1073 K for $MgCr_2O_4$, 573–1173 K for $MgFe_2O_4$ and at a temperature of 773 K and 973 K for the equimolar spinel solid solutions. The heating time was 7 h and the gas introduced into the furnace contained 13 vol.% of SO_2 and air. To determine the concentration of SO_2 in the gaseous mixture, Reich's method was applied, which involves chemisorption of SO_2 contained in a particular volume of the analysed gas in a known volume of standard iodine solution in relation to starch as an indicator, until it is coloured. By determining the concentration of SO_2 in the gas entering the reactor and in the gas leaving the reactor, at the defined reactor temperature, the conversion of SO_2 into SO_3 was calculated within a temperature range of 573–1273 K. This allowed determining the real composition of the gaseous phase versus the reactor temperature.

IV. Results and discussion

4.1. Theoretical calculations

The calculated values of standard enthalpies Δg^Θ_T of the reactions 1–6 have been presented in Fig. 1. A chem-
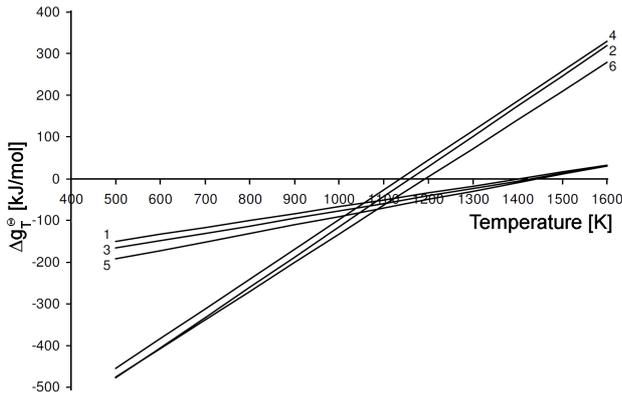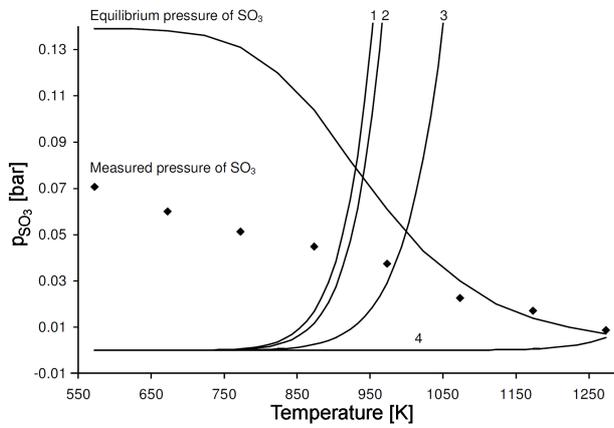
Figure 1. Standard enthalpies of the reactions 1–6

Figure 2. Dissociation pressure of Al$_2$(SO$_4$)$_3$ – 1, Cr$_2$(SO$_4$)$_3$ – 2, Fe$_2$(SO$_4$)$_3$ – 3 and MgSO$_4$ – 4, equilibrium and measured partial pressure of SO$_3$ in the reactor

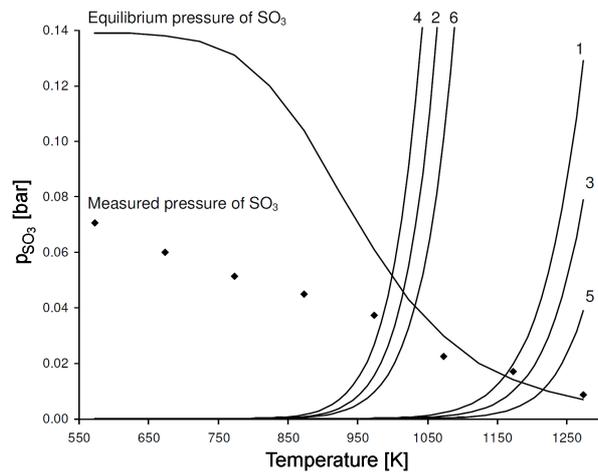**Figure 3. Equilibrium partial pressure $p^*_{SO_3}$ for the reactions 1–6, as well as SO$_3$ equilibrium and measured partial pressure in the reactor**

ical reaction will occur spontaneously when its real (and standard) free enthalpy is lower than zero ($\Delta g < \Delta g^\Theta < 0$). The calculations indicate that under standard conditions the reaction 1, 2, 3, 4, 5 and 6 will be spontaneous for temperatures <1400 K, <1150 K, <1400 K, <1140 K, <1450 K and <1190 K, respectively.

Figure 2 presents dissociation pressures of MgSO$_4$, Al$_2$(SO$_4$)$_3$, Cr$_2$(SO$_4$)$_3$ and Fe$_2$(SO$_4$)$_3$, and the equilibrium as well as measured partial pressure of SO$_3$ ($p^*_{SO_3}$), in the reactor for the reaction 2 SO$_2$ + O$_2$ $\rightleftharpoons$ 2 SO$_3$, versus temperature. Figure 3 presents a dependence of SO$_3$ partial pressure for the reactions 1–6 as well as the equilibrium and measured SO$_3$ partial pressure ($p^*_{SO_3}$) for the reaction 2 SO$_2$ + O$_2$ $\rightleftharpoons$ 2 SO$_3$ (for 13 vol.% of SO$_2$) versus temperature in the reactor.

A comparison of conditions resulting from the equilibrium state of the reaction 2 SO$_2$ + O$_2$ $\rightleftharpoons$ 2 SO$_3$ and the real conditions in the reactor indicates that the real partial pressure of SO$_3$ in the reactor is lower than the pressure resulting from the state of equilibrium of SO$_2$ oxidation to SO$_3$. As the temperature increases, SO$_3$ partial pressure in the reactor drops. Only when the temperature exceeds 1173 K, the equilibrium of this reaction is achieved in the gas flowing through the reactor.

The known values of sulphates dissociation pressures $p^*_{SO_3}$ presented in Fig. 2, allow determining the thermodynamic stability conditions for particular sulphates. The real free enthalpy Δg, of the reaction of decomposition of sulphates (MgSO$_4$, Al$_2$(SO$_4$)$_3$, Fe$_2$(SO$_4$)$_3$, Cr$_2$(SO$_4$)$_3$) is correlated with the $p^*_{SO_3}$ value in the following way:

$$\Delta g = RT \ln \left(\frac{p_{SO_3}}{p^*_{SO_3}} \right)^{\Delta \nu_g} \qquad (25)$$

where: p_{SO_3} is current partial pressure of SO$_3$ in a gaseous phase, $p^*_{SO_3}$ is sulphate dissociation pressure and $\Delta \nu_g$ is change of the number of gaseous reagents ($\Delta \nu_g > 0$). Therefore: i) if $p_{SO_3} > p^*_{SO_3}$ then $\Delta g > 0$, and equilibrium is shifted towards reactant - sulphate of the metal; ii) if $p_{SO_3} = p^*_{SO_3}$ then $\Delta g = 0$, and the reaction is in the state of equilibrium, i.e. both the oxide and sulphate of the metal will be stable; iii) if $p_{SO_3} < p^*_{SO_3}$ then $\Delta g < 0$ and the reaction equilibrium is shifted towards product - metal oxide.

A comparison of the calculated dissociation pressures of particular sulphates with an equilibrium concentration of SO$_3$ in the gaseous mixture allows us to assume that (providing the reaction of SO$_2$ oxidation to SO$_3$ in the gaseous mixture has reached an equilibrium state): MgSO$_4$ is stable throughout the considered temperature range, i.e. 573–1273 K, Cr$_2$(SO$_4$)$_3$ is stable until reaching a temperature of 1000 K, whereas Fe$_2$(SO$_4$)$_3$ and Al$_2$(SO$_4$)$_3$ are stable as long as the temperature does not exceed 930 K. When we take into consideration the real partial pressure $p^*_{SO_3}$ in the reactor under the experimental conditions, the area of MgSO$_4$ stability will be unchanged ($T < 1273$ K), whereas the areas of other sulphates stability will be shifted towards lower temperatures. Thus, Cr$_2$(SO$_4$)$_3$ will be stable until the temperature of 980 K is reached, whereas Fe$_2$(SO$_4$)$_3$ and Al$_2$(SO$_4$)$_3$ are stable as long as the temperature does not exceed 920 K and 910 K, respectively. An analysis of

Table 1. Areas of products stability of reactions between particular spinels and SO$_3$
determined for the real conditions in the reactor (R is Al, Fe, Cr)

Spinel	Area of stability		
	MgSO$_4$ + R$_2$(SO$_4$)$_3$	MgSO$_4$ + R$_2$O$_3$	MgO + R$_2$O$_3$
MgAl$_2$O$_4$	T <910 K	910 K <T <1180 K	T >1180 K
MgFe$_2$O$_4$	T <920 K	920 K <T <1240 K	T >1240 K
MgCr$_2$O$_4$	T <980 K	980 K <T <1160 K	T >1160 K

the data shown in Fig. 3, presenting the equilibrium partial pressures $p^*_{SO_3}$ for the reactions of the magnesium spinels with SO$_3$ suggests that as the temperature increases, for $p_{SO_3} < p^*_{SO_3}$ there are three areas ($p_{SO_3}(T)$) in which the thermodynamic equilibrium of the following reactions is achieved:

$$MgR_2O_4 + 4SO_3 \rightleftharpoons MgSO_4 + R_2(SO_4)_3 \quad (26)$$

$$MgR_2O_4 + SO_3 \rightleftharpoons MgSO_4 + R_2O_3 \quad (27)$$

$$MgR_2O_4 \rightleftharpoons MgO + R_2O_3 \quad (28)$$

where R is Al, Fe, Cr.

Therefore, in the state of thermodynamic equilibrium of the system, the composition of products depends on area ($p_{SO_3}(T)$), in which the considered system is situated. Areas of the stability of particular sulphates formed in the reactions 1–6 determined on the basis of data presented in Fig. 3 and their thermal stability (Fig. 2) have been given in Table 1. It has to be noted, however, that these data are based only on the thermodynamic analysis of the system and do not take into consideration the kinetics of chemical reactions, but merely describe the state of equilibrium.

4.2. Real conditions results

The equilibrium calculations of areas containing particular substances in the products of reactions of the spinels and equimolar solid solutions with sulphur oxides have been experimentally verified in laboratory tests. The XRD results of the phase composition deter-

mination of the spinel samples and their solid solutions after a reaction with sulphur oxides have been presented in Tables 2–5.

The XRD analysis of the phase composition of the sample MgAl$_2$O$_4$ after a chemical reaction at the temperature of 573 K and 673 K did not reveal the presence of MgSO$_4$ or Al$_2$(SO$_4$)$_3$ sulphates (Table 2).

In the case of MgFe$_2$O$_4$ spinel, MgSO$_4$ and Fe$_2$(SO$_4$)$_3$ were present at the above mentioned temperatures. Within the temperature range of 773–1172 K, all the examined spinels contained MgSO$_4$. Sulphates (R$_2$(SO$_4$)$_3$ where R is Al, Fe, Cr) were identified in the samples MgAl$_2$O$_4$ and MgCr$_2$O$_4$ after investigations carried out at 873 K, as well as in the sample MgFe$_2$O$_4$ after tests conducted at 673 K, 773 K and 873 K. This observation is consistent with the results of the thermodynamic analysis of particular sulphates thermal stability, which revealed that under experimental conditions MgSO$_4$ will be stable until the temperature of 1273 K and Cr$_2$(SO$_4$)$_3$, Fe$_2$(SO$_4$)$_3$, Al$_2$(SO$_4$)$_3$ will be stable until 980 K, 920 K, and 910 K respectively. In each case MgSO$_4$ was identified as a product of reactions of the equimolar solid solutions with sulphur oxides at the temperature of 773 K and 973 K. Sulphates (R$_2$(SO$_4$)$_3$) were not found, which is also consistent with the theoretical predictions.

V. Summary

The present paper investigates high-temperature sulphate corrosion of spinel materials containing:

Table 2. Phase composition analysis for MgAl$_2$O$_4$ spinel after a reaction with sulphur oxides
(+ stands for the substance presence in the sample, – stands for its absence)

Temperature [K]	Phase composition			
	MgAl$_2$O$_4$	MgSO$_4$	Al$_2$(SO$_4$)$_3$	Al$_2$O$_3$
573	+	–	–	–
673	+	–	–	–
773	+	+	–	–
873	+	+	+ (traces)	–
973	+	+	–	+
1073	+	+	–	+

Table 3. Phase composition analysis for MgCr$_2$O$_4$ spinel after a reaction with sulphur oxides
(+ stands for the substance presence in the sample, – stands for its absence)

Temperature [K]	Phase composition			
	MgCr$_2$O$_4$	MgSO$_4$	Cr$_2$(SO$_4$)$_3$	Cr$_2$O$_3$
773	+	+	–	+
873	+	+	+ (traces)	+
973	+	+	–	+
1073	+	+	–	+

Table 4. Phase composition analysis for MgFe₂O₄ spinel after a reaction with sulphur oxides
(+ stands for the substance presence in the sample, – stands for its absence)

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

Table 5. Phase composition analysis for spinel solid solutions after a reaction with sulphur oxides
(+ stands for the substance presence in the sample, – stands for its absence)

Spinel solid solution	Temperature [K]	Phase composition					
		$MgCrFeO_4$	$MgSO_4$	$Cr_2(SO_4)_3$	Cr_2O_3	$Fe_2(SO_4)_3$	Fe_2O_3
MgCrFeO₄	773	+	+	–	–	–	–
	973	+	+	–	+	–	+
		$MgAlCrO_4$	$MgSO_4$	$Al_2(SO_4)_3$	Al_2O_3	$Cr_2(SO_4)_3$	Cr_2O_3
MgAlCrO₄	773	+	+	–	–	–	–
	973	+	+	–	–	–	–
		$MgAlFeO_4$	$MgSO_4$	$Al_2(SO_4)_3$	Al_2O_3	$Fe_2(SO_4)_3$	Fe_2O_3
MgAlFeO₄	773	+	+	–	+	–	+
	973	+	+	–	+	–	+

$MgAl_2O_4$, $MgFe_2O_4$, $MgCr_2O_4$ and their equimolar solid solutions. The chemical reactions of $MgCr_2O_4$, $MgAl_2O_4$ and $MgFe_2O_4$ with SO_3, observed in the examined system, are thermodynamically spontaneous, which has been proved by calculating their free enthalpies within the temperature range of 573–1173 K. The real partial pressure of SO_3 in the reactor was lower than the equilibrium pressure $p^*_{SO_3}$ approximately till 1173 K. It was also found that as the temperature increased, the partial pressure of SO_3 in the reactor considerably decreased.

Experimental investigations of the resistance of the spinels and their solid solutions to the effect of sulphur oxides confirmed the correctness of thermodynamic calculations. The presence of $Cr_2(SO_4)_3$ was observed at 873 K, below the decomposition temperature, which is 980 K. The presence of $Fe_2(SO_4)_3$ was noted at 573 K, 673 K, 773 K and 873 K, below the decomposition temperature, reaching 920 K, $Al_2(SO_4)_3$ was found at 873 K, also below the decomposition temperature, which is 910 K. The most stable $MgSO_4$ (up to 1273 K) was identified throughout the whole examined temperature range for chromium and iron spinel as well as spinel solid solutions. The absence of $MgSO_4$ in the products of alumina spinel reactions at the temperature of 573 K and 673 K can be explained by the reaction kinetics. The rate of $MgSO_4$ formation in these conditions is most probably too low to provide tangible amounts of this product of reaction during the experiment. The absence of sulphates ($R_2(SO_4)_3$ where R is Al, Fe, Cr) in the reaction products below the predicted temperature of

their decomposition can be explained in a similar way.

The conducted investigations and thermodynamic considerations have allowed identifying chemical reactions which will occur at elevated temperatures in spinel materials having contact with sulphur oxides. The corrosion of spinels in basic refractories exposed to $SO_2−O_2−SO_3$ atmosphere is driven by $MgSO_4$ and R_2O_3 (R is Al, Fe, Cr) formation leading to spinel dissociation. At lower temperature, traces of $R_2(SO_4)_3$ sulphates can be formed.

References

1. J.R. Hill, J.R. Craig, G.V. Gibbs, "Systematic of the spinel structure type", *Phys. Chem. Miner.*, **4** (1979) 317–339.

2. R. Sridhar, J.M. Toguri, S.R. Simeonov, "Thermodynamic conideration in copper pyrometallurgy", *JOM (Journal of The Minerals, Metals & Materials Society)*, **49** (1997) 48–52.

3. S.R. Simeonov, R. Sridhar, J.M. Toguri, "Sulfide capacities of fayalite - base slag", *Metall. Trans. B*, **26** (1995) 325–333.

4. G.A. Meyer, J.S. Warner, Y.K. Rao, H.H. Kellog, "Thermodynamic properties of molten sulfides: Part I The system Ni-S", *Metall. Trans. B*, **6** (1975) 229–235.

5. J. Wojsa, *Basic Unshaped Refractory Materials (in*

Polish), Institute of Ceramics and Building Materials, Refractory Materials Division in Gliwice, Gliwice, Poland, 2009

6. J. Wojsa, T. Trochimowicz, T. Ostrowski, "Współczesne kryteria oceny wyrobów zasadowych do konwertorów miedziowych (The current criteria for assessment of basic refractoriness to copper converters)", *Ceramika*, **88** (2005) 79–87.

7. M. Köffel, T. Taschler, "Refractories for the copper and lead industry", *World Metall. Erzmetall*, **59** [3] (2006) 133–142.

8. C.A. Rodriguez Gonzalez, W.F. Caley, R.A.L. Drew, "Copper matte penetration resistance of basic refractories", *Metall. Mat. Trans. B*, **38** (2007) 167–174.

9. J.L. Liow, P. Tsirikis, N.B. Gray, "Study of refractory wear in the tuyere region of a Peirce-Smith nickel convertor", *Canad. Metall. Q*, **37** [2] (1998) 99–117.

10. R. McPherson, "Magnesium sulfate formation in the basic linings of copper smelting furnace", *Bull. Am. Ceram. Soc.*, **48** (1969) 791–793.

11. G.R. Rigby, "A study of basic brick from various copper smelting furnaces", *Trans. AIME*, **224** (1962) 887–892.

12. M. Makipaa, P. Taskinen, "Refractory wear in copper converters: Part I: Blister copper-refractory Interactions", *Scand. J. Metall.*, **9** (1980) 273–281.

13. M. Makipaa, P. Taskinen, "Refractory wear in copper converters: Part II: Blister copper-refractory interactions", *Scand. J. Metall.*, **22** (1993) 203–212.

14. N.Z. Fotoyi, R.H. Eric, "Interaction of MgO-MgR$_2$O$_4$ (R: Al, Cr, Fe) refractories with SO$_2$-containing gases", pp. 373–385 in *Southern African Pyrometallurgy*. Eds. R.T. Jones P. den Hoed, Southern African Institute of Mining and Metallurgy, Johannesburg, South Africa, 2011.

15. N.Z. Fotoyi, *Gas-refractory Interactions of Basic Refractories with Sulfur-bearing Gases Produced in Converter Furnaces during Extraction of Platinum Group Metals in Non-ferrous Industry*, M.Sc. Dissertation, University of the Witwatersrand, Johannesburg, South Africa, 2009.

16. J. Podwórny, *Studies on the Kinetics and Mechanism of Topochemical Reaction in the System MgO-spinel MgR$_2$O$_4$-SO$_2$-O$_2$* (in Polish), Ph.D. Dissertation, Silesian University of Technology, Faculty of Chemistry, Gliwice, Poland, 2001.

17. J. Podwórny, J. Piotrowski, J. Wojsa, "Investigations into kinetics and mechanism of gas-solid state processes in MgO–MgR$_2$O$_4$ (R: Al, Cr, Fe) spinels–SO$_2$–O$_2$ system", *Ceram. Int.*, **34** (2008) 1587–1593.

18. J. Barin, *Thermochemical Data of Pure Substances*, VCH Verlagsgesellschaft, Weinheim, Germany, 1989.