



# Refractories from the MgO-Al<sub>2</sub>O<sub>3</sub>-SnO<sub>2</sub> System for Metallurgical Applications

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## Abstract

Due to the excellent corrosion resistance and high durability, chrome containing refractories are broadly used in many branches of modern industry. However, among different types of refractory waste, chrome-containing materials after service are probably the most dangerous, requiring complex and expensive treatment before further processing. Due to the potential hazards from refractory waste and changes in technical preferences of the users, the share of chromium containing materials in the total production of refractories has been systematically decreasing. Searching for the chrome-free alternatives, fundamental properties of materials from the MgO-Al<sub>2</sub>O<sub>3</sub>-SnO<sub>2</sub> system, *i.e.*, phase composition and thermal stability, were studied. On that basis three different kinds of SnO<sub>2</sub>-containing refractories were prepared, *i.e.*, fired bricks, chemically bonded and hydraulically bonded materials. The microstructure and basic properties of the developed refractories were investigated. The results obtained so far seem to be promising and confirm the possibility of applying of selected materials in low temperature processes as an alternative to typically used fired magnesia-chromite products.

**Keywords:** MgO-Al<sub>2</sub>O<sub>3</sub>-SnO<sub>2</sub> system, Basic refractories, Chrome-free refractories

## MATERIAŁY OGNIOTRWALE Z UKŁADU MgO-Al<sub>2</sub>O<sub>3</sub>-SnO<sub>2</sub> DO ZASTOSOWAŃ METALURGICZNYCH

Materiały ogniotrwałe zawierające chrom wykorzystywane są szeroko w wielu gałęziach współczesnego przemysłu w związku z ich doskonałą odpornością korozyjną i wysoką trwałością. Jednakże, wśród wielu rodzajów odpadów materiałów ogniotwałych zużyte materiały zawierające chrom należą do najbardziej niebezpiecznych i wymagają złożonej i drogiej obróbki przed dalszym przetwarzaniem. W związku z potencjalnym ryzykiem niesionym przez odpady ogniotrwałe oraz ze zmianami w technicznych preferencjach użytkowników, udział materiałów zawierających chrom w całkowitej produkcji wyrobów ogniotwałych systematycznie zmniejsza się. Poszukując alternatywnych, bezchromowych materiałów zbadano podstawowe właściwości materiałów z układu MgO-Al<sub>2</sub>O<sub>3</sub>-SnO<sub>2</sub>, tj. skład fazowy i stabilność termiczną. Na tej podstawie przygotowano trzy różne rodzaje materiałów ogniotwałych zawierających SnO<sub>2</sub>, a mianowicie: cegły wypalane, materiały wiązane chemicznie i hydraulicznie. Zbadano mikrostrukturę i podstawowe właściwości opracowanych materiałów. Dotychczas uzyskane wyniki są obiecujące i potwierdzają możliwość zastosowania wybranych materiałów w procesach niskotemperaturowych, jako alternatywę dla typowo wykorzystywanych, wypalanych produktów magnezowo-chromitowych.

**Słowa kluczowe:** układ MgO-Al<sub>2</sub>O<sub>3</sub>-SnO<sub>2</sub>, materiały ogniotrwałe zasadowe, materiały ogniotrwałe bezchromowe

## 1. Introduction

The research and development of new refractory materials is strictly connected with technological requirements of the producers and users as well as the new legal regulations due to environmental and human health protection. This relation can be readily noticeable in refractory materials for copper metallurgy. The working linings of different thermal units in this branch of industry are made of magnesia-chromite bricks containing 18-35 % Cr<sub>2</sub>O<sub>3</sub> [1-3]. Unfortunately, this kind of refractory materials after service is characterized by a relatively high concentration of carcinogenic and toxic Cr(VI) compounds [4-6]. Due to the potential hazards from chrome-containing waste a tendency to use alternative, chrome-free refractories has been observed for many years. The elimination of chrome oxide is still one of the most important objectives of many research attempts in the basic refractories branch. However, as distinct from steel,

glass and cement industries, the copper metallurgy is the area where replacement of typically used magnesite-chrome materials demands further investigations and studies [3, 5, 7, 8]. Accordingly, attempts were undertaken to develop new, alternative materials in which cassiterite (SnO<sub>2</sub>) was used as a spinel forming agent.

This work summarizes the results of investigations into the properties of materials from the MgO-Al<sub>2</sub>O<sub>3</sub>-SnO<sub>2</sub> system, including phase composition studies and thermal analysis. On this basis different types of cassiterite-containing refractory materials were prepared and characterised. In the case of fired magnesia bricks modified with SnO<sub>2</sub>, the results obtained so far seem to be promising. The properties of unfired materials also confirm the possibility of the application new materials in low temperature processes, especially in the copper industry, as an alternative to the typically used fired magnesia-chromite products.

## 2. Experimental

### 2.1. Raw materials

The samples for thermal analysis and phase composition investigations were prepared from following commercial powders:

- pure MgO, containing over 98 % MgO (after firing at 500°C for 1 h),
- fused magnesia-alumina spinel (MA), containing 72 % Al<sub>2</sub>O<sub>3</sub>,
- extra pure SnO<sub>2</sub>, containing over 99 % SnO<sub>2</sub>.

Three commercial raw materials were used to prepare the refractory samples for microstructure investigations and research into material properties:

- fused MA spinel, containing 72 % Al<sub>2</sub>O<sub>3</sub>,
- magnesia clinker, containing 98 % MgO,
- SnO<sub>2</sub> powder, containing 90 % SnO<sub>2</sub>.

Magnesia-cassiterite co-clinkier was also used as an alternative source of SnO<sub>2</sub>.

Water solutions of sulfite lye and magnesium sulphate were used as binders for fired and chemically bonded materials, respectively.

The following additives were used to prepare hydraulically bonded spinel-cassiterite materials:

- Al<sub>2</sub>O<sub>3</sub> and microsilica powders,
- high-alumina cement,
- reinforcing steel fibres,
- fluidizing agent (sodium tripoliphosphate).

### 2.2. Preparation of samples and range of investigations

Powder mixtures for thermal analysis were prepared in a magnetic laboratory mill by homogenization of components in ethyl alcohol for 2 h at 70-75°C. After drying, in order to remove the organic components, the mixtures were kept at 500°C for 1 h. A thermal analysis of the prepared powder mixtures for 5 h at 1500°C was conducted, using NETZSCH-STA409 apparatus.

Phase composition studies were conducted using analogically prepared powder mixtures of the same starting materials. After drying, the 6 % solution of PVA in amount of 4 % was added as a binder and pellets of 20 mm in diameter and 5 mm height were pressed at 100-120 MPa. The analysis of phase composition after firing at different temperatures was carried out by means of Philips-X'Change using the Rietveld method.

The samples of fired and chemically bonded refractory materials were prepared by mixing grain fractions of raw materials with a binder (3.5-4 %) and powder components. Next at 120 MPa pressure, two types of samples were formed: bricks of 60x120x240 mm (fired materials) and cylinders of  $f = h = 50$  mm (chemically bonded materials). In the former case, the materials were prepared in industrial conditions. After drying, the samples were fired at different temperatures with different soaking time.

SnO<sub>2</sub>-modified spinel castables were prepared by vibrocasting of homogenous mixtures of aggregates, powder components, reinforcing fibres and water (5-6 %). After drying and firing at different temperatures, the samples for

respective investigations were cut out of previously prepared 60x60x240 mm bars.

The microstructure investigations, *i.e.*, optic microscopy and SEM were performed using a REICHERT-MeF2 camera microscope and a JEOL-ISM-35 scanning microscope, respectively. Pore size distribution was determined using a mercury porosimeter AUTOPORE 9500 of MICROMERITICS and the analysis of phase composition after firing was carried out by means of Philips-X'Change X-ray diffractometer, using Rietveld method.

The samples of fired refractories for corrosion resistance tests were cut out of the bricks obtained in industrial conditions. In the case of unfired materials the samples were prepared in laboratory conditions. The previously prepared crucibles filled with a corrosive agent (glass batch, anode copper, slag from copper converter and slag from anode furnace) were fired for 6-8 h at 1300-1400°C. After the tests, the infiltration ratio of corrosive agent was determined and compared to the reference materials, *i.e.*, typical magnesia-chromite (MC) and magnesia (M) bricks.

## 3. Results and discussion

### 3.1. Phase composition and thermal analysis

The results of thermal analysis of powder mixtures containing tin dioxide, presented in Fig. 1 and Table 1, showed that the well known phenomenon of SnO<sub>2</sub> evaporation at high temperatures can be considerably limited in the mixtures containing MgO, probably due to the formation of magnesium orthostannate (Mg<sub>2</sub>SnO<sub>4</sub>). For the materials containing tin dioxide, relatively high mass loses, due to SnO<sub>2</sub> evaporation, have one fundamental implication, *i.e.*, a limited to reasonable level temperature of heat treatment. The same applies to the maximum working temperature of SnO<sub>2</sub>-containing refractories.

The results of phase composition investigations of the materials from MgO-Al<sub>2</sub>O<sub>3</sub>-SnO<sub>2</sub> system after firing for 3 h at 1500°C are presented in Fig. 2. The starting composition of the investigated samples and most important features of their phase composition are shown on the background of the ternary MgO-Al<sub>2</sub>O<sub>3</sub>-SnO<sub>2</sub> phase diagram [9].

Table 1. Results of thermogravimetric analysis.

Sample #	Composition	$\Delta m_{1500^\circ\text{C}}$ [%]	$\Delta m'$ [%]
1	50 % MgO - 50 % SnO <sub>2</sub>	-7.67	-15.34
2	70 % MgAl <sub>2</sub> O <sub>4</sub> - 30 % SnO <sub>2</sub>	-12.03	-40.01
3	40 % MgAl <sub>2</sub> O <sub>4</sub> - 30 % MgO - 30 % SnO <sub>2</sub>	-5.38	-17.93

$$\Delta m' = (\Delta m / \text{SnO}_2 \text{ content}) \times 100 \%$$

The presented results suggest that the state of equilibrium was not achieved in each case, which is confirmed by the presence of amorphous phase of unknown composition. The composition of this phase cannot be determined by

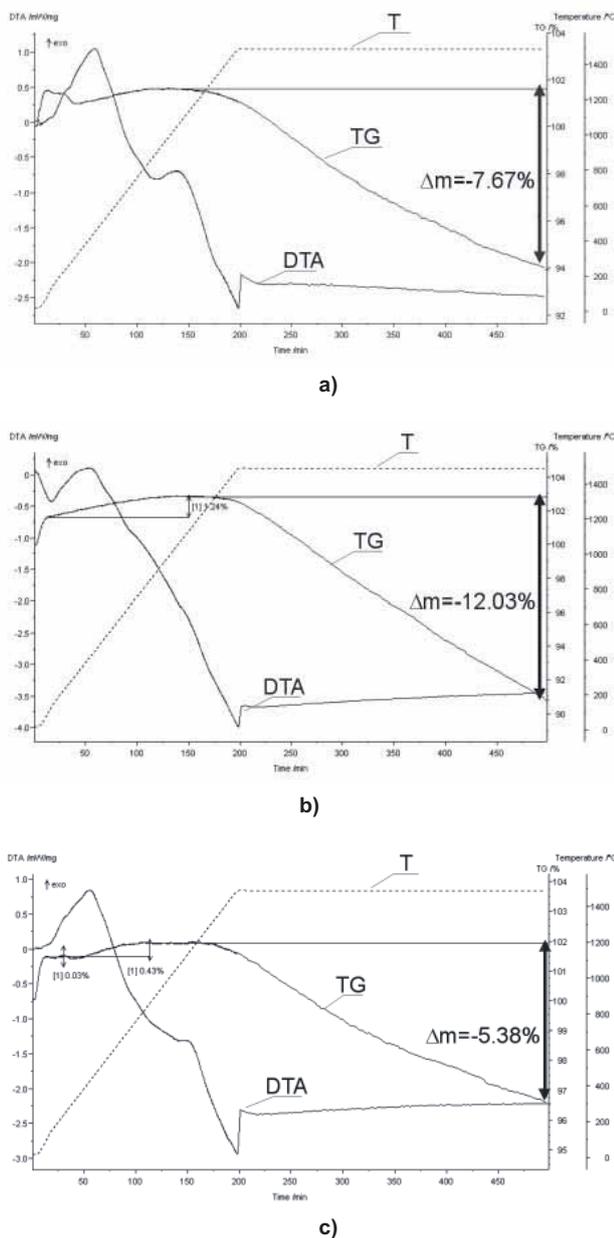
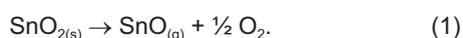


Fig. 1. Results of thermal analysis of powder samples containing tin dioxide: a) 50 % MgO - 50 % SnO<sub>2</sub>, b) 70 % MgAl<sub>2</sub>O<sub>4</sub> - 30 % SnO<sub>2</sub>, c) 40 % MgAl<sub>2</sub>O<sub>4</sub> - 30 % MgO - 30 % SnO<sub>2</sub>.

means of simple stoichiometric calculations, due to SnO<sub>2</sub> evaporation at higher temperatures [10, 11].

The results of SEM analysis (Fig. 3) reveal the presence of isomorphic grains of magnesium orthostannate (Mg<sub>2</sub>SnO<sub>4</sub>) and blurred grain boundaries, indicating possible crystal structure differences in these areas. The existence of amorphous phase after firing the material at high temperatures (Table 2) shows the possibility of stoichiometry deviation, due to SnO<sub>2</sub> evaporation from the grain boundaries, according to the reaction:



As it is suggested, SnO<sub>2</sub> evaporation probably leads to slight differences in the chemical composition between grains and grain boundaries [10]. Consequently, a local distortion of Mg<sub>2</sub>SnO<sub>4</sub> crystal lattice may be expected, leading to a creation of locally disordered material which is most probably detected as an amorphous phase. Moreover, the

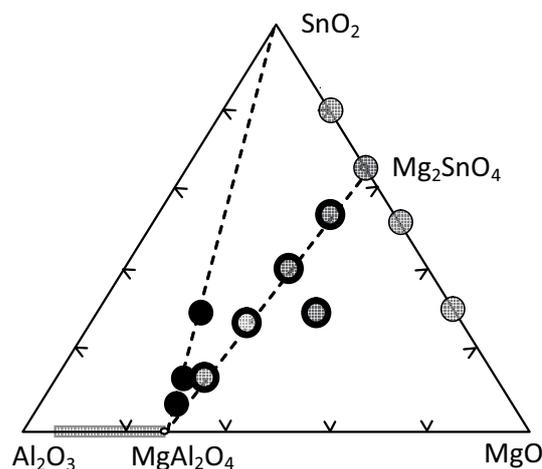


Fig. 2. The ternary MgO-Al<sub>2</sub>O<sub>3</sub>-SnO<sub>2</sub> phase diagram and results of phase composition investigations.

phase composition analysis revealed the presence of solid solutions in MgAl<sub>2</sub>O<sub>4</sub>-Mg<sub>2</sub>SnO<sub>4</sub> series with a broad range of existence. The results of phase composition and thermal analysis reveal that the synthesis of magnesium orthostannate takes place even below 1000°C.

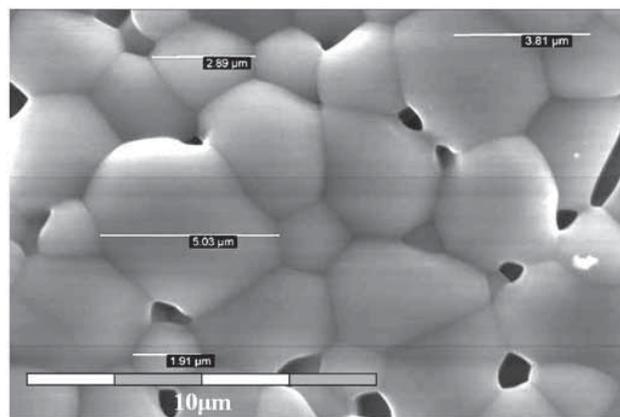


Fig. 3. SEM image of sample containing 35 % MgO and 65 % SnO<sub>2</sub> after firing at 1500°C.

Table 2. Phase composition of samples containing 35 % MgO and 65 % SnO<sub>2</sub> after firing for 3 h at indicated temperatures.

Firing temperature [°C]	Contents [%]			
	MgO	SnO <sub>2</sub>	Mg <sub>2</sub> SnO <sub>4</sub>	Amorphous phase
1000	31.5	57.1	9.5	2.0
1100	15.2	27.1	55.3	2.4
1200	5.2	10.1	68.1	16.5
1350	-	3.1	75.5	21.4
1500	-	1.1	80.6	18.2

### 3.2. Fired refractories

Due to easy evaporation of SnO<sub>2</sub> at high temperatures, its share in fired refractories should be limited to a reasonable amount. Another method of SnO<sub>2</sub> losses prevention consists in an application of this modifier in a form of MgO-SnO<sub>2</sub> co-clinker. The problem of SnO<sub>2</sub> evaporation is not as

much relevant in case of unfired materials, *i.e.*, chemically and hydraulically bonded.

The overview of different properties of SnO<sub>2</sub>-containing fired materials prepared in industrial conditions is shown in Table 3.

Table 3. Properties of the developed basic refractories prepared in industrial conditions.

Type of material		MA-SnO <sub>2</sub>	M-SnO <sub>2</sub>
Firing temperature	[°C]	1600	1650
Firing shrinkage	[%]	<i>a</i>	+0.26
		<i>l</i>	+0.09
Open porosity	[%]	15.6	13.3
Apparent density	[g/cm <sup>3</sup> ]	3.07	3.11
Crushing strength	[MPa]	51.7	58.2
Modulus of rupture	[MPa]	20°C	9.8
		1450°C	3.9
Thermal shock resistance 1000°C/ water	temperature changes	8	7
Refractoriness under load	[°C] T <sub>0.6</sub>	>1700	>1700
Thermal expansion coefficient (20-1000°C)	[1/K]·10 <sup>-6</sup>	8.8	13.5
Work of fracture at 20°C (g <sub>wof</sub> )	[J/m <sup>2</sup> ]	32.2	80.0
Gas permeability	[nperm]	4.02	4.11
Phase composition:			
MgAl <sub>2</sub> O <sub>4</sub>		++	-
SnO <sub>2</sub>		+	-
CaSnO <sub>3</sub>		+	+
Mg <sub>2</sub> SnO <sub>4</sub>		++	++
MgO		-	++
Amorphous phase		-	+

Apart from the physical properties of spinel-cassiterite (MA-SnO<sub>2</sub>) and magnesia-cassiterite (M-SnO<sub>2</sub>) fired refractories, the results of phase composition analysis are presented. Microstructure images of developed refractories are shown in Fig. 4. Mercury porosimetry revealed a favorable pore size distribution of developed materials with the median pore diameter not larger than 9 μm.

The results of thermal analysis have proved relatively high mass losses of the materials from the MgO-Al<sub>2</sub>O<sub>3</sub>-SnO<sub>2</sub> system, due to SnO<sub>2</sub> evaporation. Then, the properties of spinel-cassiterite and magnesia-cassiterite fired refractories are even more surprising (Table 3). In fact, all the characteristics are satisfactory, and compared to the reference

Table 4. Infiltration ratio of the developed basic refractories and reference products after static corrosion resistance tests. Reference products: MC – fired magnesia-chromite brick, M – fired magnesia brick.

Corroding agent	Infiltration ratio [%]			
	Reference products		Developed materials	
	MC	M	MA-SnO <sub>2</sub>	M-SnO <sub>2</sub>
Anode copper	53.5	–	30.6	19.5
Converter slag	89.4	–	84.5	67.9
Molten glass	–	78.5	49.4	72.5

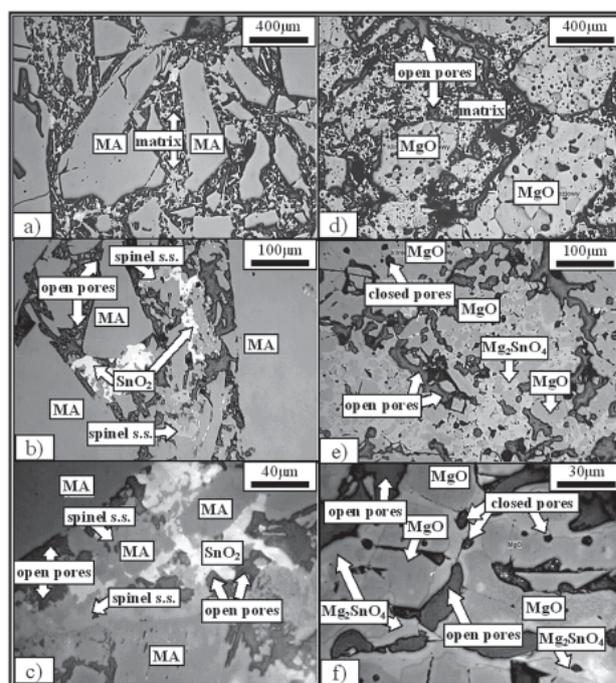


Fig. 4. Microstructure of the developed fired refractories spinel-cassiterite – MA-SnO<sub>2</sub> (a, b, c) and magnesia cassiterite – M-SnO<sub>2</sub> (d, e, f).

Table 5. Properties of SnO<sub>2</sub>-modified, unfired refractories manufactured in the laboratory at indicated conditions.

Type of material		M-SnO <sub>2</sub> chemically bonded	MA-SnO <sub>2</sub> hydraulically bonded
20°C/48h			
Apparent density	[g/cm <sup>3</sup> ]	-	3.06
Crushing strength	[MPa]	-	28.8
150°C/4h			
Apparent density	[g/cm <sup>3</sup> ]	2.88	3.06
Crushing strength	[MPa]	42.2	101.3
800°C/4h			
Apparent density	[g/cm <sup>3</sup> ]	2.82	2.96
Open porosity	[%]	18.7	17.3
Crushing strength	[MPa]	27.9	84.8
1200°C/4h			
Firing shrinkage	[%]	0.15	0.3
Apparent density	[g/cm <sup>3</sup> ]	2.80	2.96
Open porosity	[%]	19.6	18.6
Crushing strength	[MPa]	29.2	97.2
Thermal shock resistance 1000°C/ water	temperature changes	4	>30
1400°C/4h			
Firing shrinkage	[%]	0.10	0.30
Apparent density	[g/cm <sup>3</sup> ]	2.82	2.99
Open porosity	[%]	18.9	16.7
Crushing strength	[MPa]	55.2	70.4
Thermal shock resistance 1000°C/ water	temperature changes	6	14
Phase composition:			
magnesia-alumina spinel - MgAl <sub>2</sub> O <sub>4</sub>			++
cassiterite - SnO <sub>2</sub>			+
anorthite - CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>			+
corundum - α-Al <sub>2</sub> O <sub>3</sub>			+

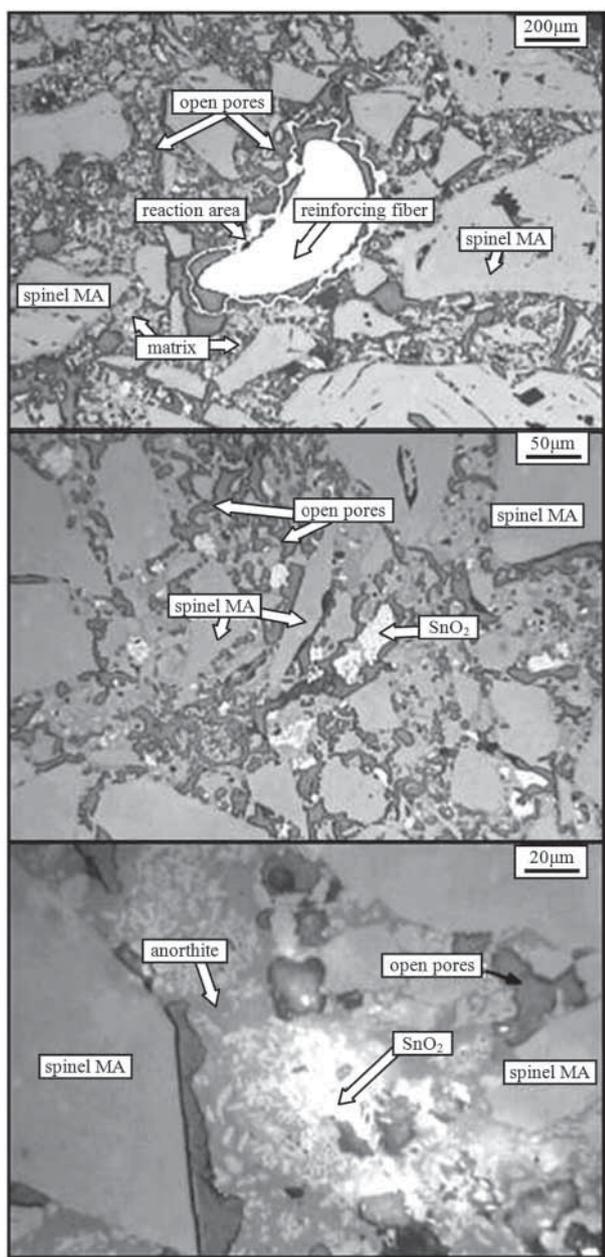


Fig. 5. Microstructure of the developed,  $\text{SnO}_2$ -modified spinel castable heat treated at  $1400^\circ\text{C}$ .

materials, the results of corrosion resistance tests deserve special attention (Table 4). These results were considered promising, to say the least.

Taking into account the basic properties, the results of microstructure investigations and static corrosion resistance tests were selected for further industrial trials with the magnesia-cassiterite type material ( $\text{M-SnO}_2$ ). One ton of  $350 \times 75 \times 150$  mm bricks were mounted in a copper metallurgy plant in the gas zone of an anode hearth furnace about 1.5 m above the liquid metal line. Durability of the bricks was 12 months or 350 heat cycles, being equal to the service life of typical magnesia-chromite materials, usually applied in this zone.

### 3.3. Unfired refractories

As it was stated before, the undesired loss of  $\text{SnO}_2$ , due to its evaporation, refers primarily to the fired refractories

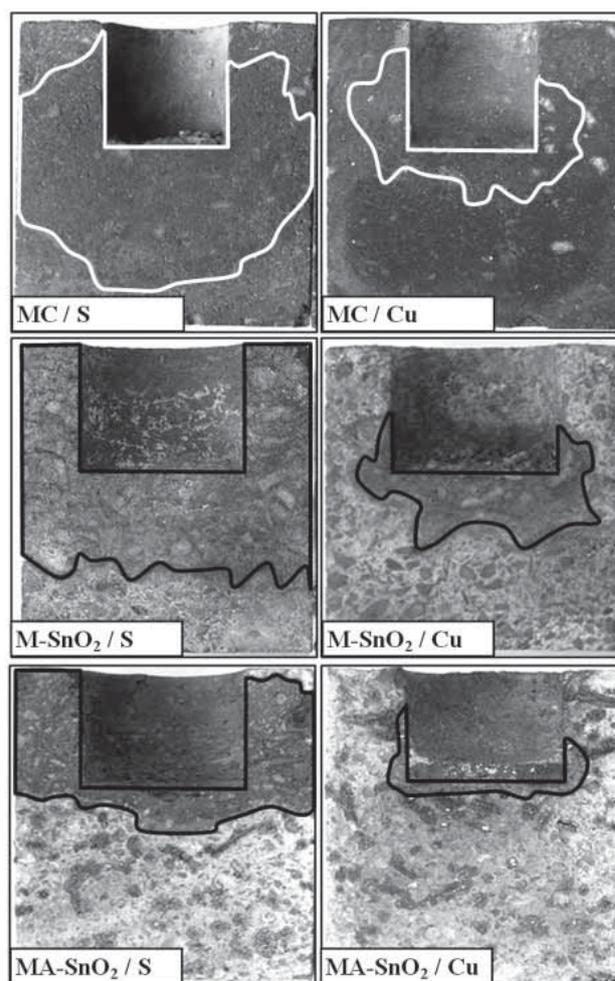


Fig. 6. Images of reference product (MC) and developed materials after corrosion resistance tests: MC – reference, magnesia-chromite brick,  $\text{M-SnO}_2$  - developed chemically bonded material,  $\text{MA-SnO}_2$  - developed spinel castable, Cu - anode copper, S - anode furnace slag.

and is not as much relevant in case of the unfired materials. Consequently, two other types of  $\text{SnO}_2$ -containing materials were investigated, *i.e.*, chemically bonded magnesia-based ( $\text{M-SnO}_2$ ) and hydraulically bonded spinel-based ( $\text{MA-SnO}_2$ ). In Table 5, the overview of properties of the samples prepared in laboratory conditions has been given. In the case of  $\text{SnO}_2$ -modified spinel castable, the results of phase composition analysis are also presented.

Microstructure investigations of the developed spinel castable after heat treating at  $1400^\circ\text{C}$  revealed the presence of magnesia-alumina spinel grains in a homogenous, multicomponent matrix consisted of fine MA grains as well as anorthite, cassiterite and corundum aggregates (Fig. 5). The median pore diameter of developed castable does not exceed  $2.6 \mu\text{m}$ .

Static corrosion resistance tests were conducted for both materials, using the samples fired previously at  $1200^\circ\text{C}$ . Anode copper slag and anode furnace one were used as corrosive agents. The results of conducted tests reveal a considerably lower infiltration ratio of developed spinel castable compared to reference material (high grade magnesia-chromite brick). In the case of the chemically bonded,  $\text{SnO}_2$ -modified material, the infiltration ratio was similar to the reference product (Fig. 6). The results of analogous tests for

materials varying only in SnO<sub>2</sub> content reveal a general correlation: the higher SnO<sub>2</sub> content the lower infiltration ratio.

The properties of developed spinel castable seem to be even more promising than that of fired magnesia-cassiterite material which, with satisfying results, was already tested in industrial conditions. Consequently, this work indicates the principal directions of further investigations of monolithic, SnO<sub>2</sub>-containing materials, involving, *e.g.*, studies of high temperatures interaction between individual components as well as between components and corrosive agents, optimisation of material composition and, at last, the trial tests in selected metallurgical application.

All developed SnO<sub>2</sub>-containing refractory materials display satisfactory basic properties and better (or at least equal) corrosion resistance as compared to typical magnesia-chromite refractories. It must be underlined that owing to the lack of high temperature heat treatment, chemically and hydraulically bonded materials containing tin dioxide have two fundamental advantages comparing to fired refractories, *i.e.*, considerably lower manufacturing costs and absence of undesired SnO<sub>2</sub> losses. For this reason, further investigations of both unfired, SnO<sub>2</sub>-modified materials including trial tests are in progress.

#### 4. Conclusions

Fundamental properties of materials from the MgO-Al<sub>2</sub>O<sub>3</sub>-SnO<sub>2</sub> system were characterised and summarized. The results of thermal and phase composition analyses confirm that MgO reduces the volatility of SnO<sub>2</sub> at high temperatures, probably due to Mg<sub>2</sub>SnO<sub>4</sub> formation. The amorphous phase detected in the samples containing both MgO and SnO<sub>2</sub> was attributed to the lack of equilibrium state and the formation of disordered, metastable phase, probably due to preferential SnO<sub>2</sub> evaporation from grain boundaries. The complex phase characteristics of materials from the MgO-Al<sub>2</sub>O<sub>3</sub>-SnO<sub>2</sub> system demand further research attempts comprising, *e.g.*, amorphous phase composition studies.

Three different types of SnO<sub>2</sub>-modified refractory materials were developed and characterised. The results obtained so far, especially in the case of fired magnesia-cassiterite and hydraulically bonded spinel-cassiterite materials seem to be at least promising. In the laboratory tests both types

of cassiterite-containing materials have shown higher corrosion resistance in comparison to the top grade, magnesia-chromite reference product. The industrial test results seem to confirm the expectations connected with the new solution as a real alternative to chromia-containing, materials used in low-temperature processes. This conclusion needs special attention in relation to copper metallurgy, where developed materials may meet future demand for competitive, chrome-free refractories. For this reason, further investigations of SnO<sub>2</sub>-containing materials are in progress.

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