

SILICOTHERMIC REDUCTION PROCESS IN MAGNESIUM PRODUCTION

Thermal analysis and characterization of the slag

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In this paper there are presented the results of the characterization and thermal analysis of the slag from the magnesium plant 'Bela Stena', Serbia.

The results of X-ray fluorescence analysis, scanning electron microscopy (SEM), optical microscopy (LOM) and X-ray diffraction (XRD) were used for chemical and mineralogical analysis of the solidified slag samples. Differential thermal analysis (DTA), thermo-gravimetric (TG) analysis and thermal microscopy results were used for determination of characteristic phase transformations. The solidified slag shows dicalcium silicate based structure. Magnesium is mostly present in the form of the following minerals: periclase, merwinite and melilite.

Keywords: DTA, magnesium, SEM, silicothermic reduction, slag, XRD

Introduction

The dicalcium silicate based slag of the silicothermic reduction process of magnesium production is raw material for many industrial products as cement, glass and ceramics [1–6].

Balac [7] considered potential application of this slag for production of thermo-insulating material, Hayakawa *et al.* [8] explored capacities of the slag as reagent in steelworks, while Dunaev and Mihalevic [9] and Zuda *et al.* [10] studied characteristics of the slag.

Phase relationships in the ternary CaO–SiO₂–Al₂O₃ system were studied by Renkin and Wright [11] and Oelsen [12].

McCaffery [13] studied viscosities in this ternary system, and also Sichen and Seetharaman [14]. Thermal studies of ternary system were done by Grzeszczyk and Szuba [15] and Stoch *et al.* [16].

Thermodynamic properties of CaO–MgO–SiO₂ system are studied by Jung, Decterov and Pelton, but also by numerous authors [17–21]. Phase equilibrium and distribution of minor elements of this system are determined by Henao and Itagaki [22].

Viscosities of CaO–MgO–Al₂O₃–SiO₂ slag systems were investigated by many authors [23–25]. Thermodynamic properties of this system were investigated by Herzberg and Zhang [26] and Davies *et al.* [27]. Kinetics of the same system were studied by Sridhar and Cramb [28] and Jansson *et al.* [29] and characterization of this quaternary system was

investigated by Dahl *et al.* [30]. Hiroki and Hibeoki [31] determined activities of components in the quaternary system at 1873 K.

Dolomite as a raw material for Mg production continues to be an interesting area of investigation. Thermal characteristics of mixtures of dolomite and other minerals were studied by Kök and Smykatz-Kloss [32]. Kinetics and thermal decomposition of dolomite were investigated by Olszak-Humienik and Mozejko [33].

Dolomite treatment by silicothermic reduction process for magnesium production was studied by Morsi *et al.* [34, 35].

The aim of this work is to accomplish chemical, mineralogical and thermal analysis of the slag produced in the Magnetherm type of silicothermic reduction process in magnesium production.

Experimental

The analyzed samples of the slag were taken from the magnesium plant 'Bela Stena', Baljevac, Serbia. In the classic Magnetherm silicothermic reduction process, which is applied in this plant, sufficient alumina is added to melt the dicalcium silicate slag that is formed at approximately 1500°C. This allows the reactor to be heated by the electrical resistance of the slag and further more, allows the reaction products to be removed in the molten state. About 0.45 kg of calcined bauxite, 2.7 kg dolomite and 0.45 kg

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ferrosilicon are required for production of 0.45 kg metallic magnesium. The slag is tapped twice a day by introducing argon into the furnace for braking the vacuum. The slag outlet is electrically lanced and the molten calcium aluminum silicate is quenched into water to stabilize the slag. About 5.9 kg of slag is produced per kg magnesium.

Chemical composition of the slag was measured using X-ray fluorescence (ARL 86480).

SEM investigation was carried out on electronic microscope Philips XI-300 with EDX from EDAX, with resolution of 1 nm (30 kV) and 5 nm (1 kV), exciting voltage 0.2–30 kV, enlargement of 500000 times and detector for secondary and back electrons.

XRD analysis was used for mineralogical investigation. Samples were investigated using diffractometer Philips PW 1710 under following conditions: radiation from copper anticatode with $\text{CuK}\alpha=1.54178 \text{ \AA}$ and graphite monochromator, working voltage $U=40 \text{ kV}$, current strength $I=30 \text{ mA}$. Samples were investigated in the range of 2θ 4–90° (with step of 0.02° and time 0.8 s).

Thermal microscopy was done on LEITZ thermal microscope. The light optical microscopy was conducted on light optical microscope Carl Zeiss-Jena.

DTA-TG measurements were carried out with the DTA STA 409 (Netzsch, Germany). Sample mass was 30 mg and heating rate $10^\circ\text{C min}^{-1}$.

Results and discussion

Chemical composition analysis

Chemical compositions of the twenty slag samples were investigated using X-ray fluorescence analysis. Obtained results, including detected concentration intervals and average concentration of slag components, are shown in Table 1.

The item 'rest' includes: Zn, Cu, TiO_2 , Mn_2O_3 and SO_3 .

Table 1 Chemical composition of the slag (mass%)

Component	Concentration range/%	Average value/%
SiO_2	23.43–24.25	23.84
Al_2O_3	11.16–12.61	11.885
Fe_2O_3	0.18–0.62	0.4
CaO	51.59–52.84	52.215
MgO	7.02–8.82	7.92
Na_2O	0.34–0.39	0.365
K_2O	0.01–0.03	0.02
S	0.08–0.15	0.115
Rest	6.18–0.32	3.25

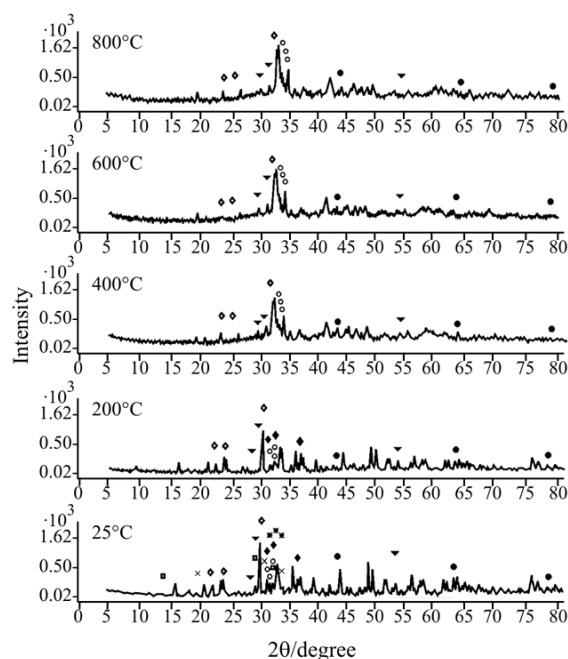


Fig. 1 X-ray diffractograms of slag samples heated at: 25, 200, 400, 600 and 800°C (\diamond – γ - CaOSiO_2 ; \bullet – periclase, \circ – merwinite, \square – hydrosilicate Ca, \blacktriangledown – melilite, \blacklozenge – diopside, $*$ – rankinite, $*$ – β - CaOSiO_2)

The average value of MgO in the slag is between 7.02 and 8.82% that indicates significant losses of magnesium with slag.

Mineralogical analysis

Mineralogical investigation of the slag was done using XRD analysis and the results are shown in Fig. 1 [36]. The samples of granulated slag were heated for 3 h at: 200, 400, 600 and 800°C, and cooled in the air to the room temperature.

Table 2 Approximated mineralogical composition of the heated slag samples (mass%)

Minerals	Approximated mineralogical composition				
	25°C	200°C	400°C	600°C	800°C
β -2CaOSiO ₂	2	–	–	–	–
γ -2CaOSiO ₂	70	71	72	70	71
Melilite	5	8	7	9	8
Merwinite	8	4	14	13	16
Periclase	9	11	7	8	5
Hydrosilicate Ca	4	–	–	–	–
Rankinite	1	–	–	–	–
Diopside	1	1	–	–	–

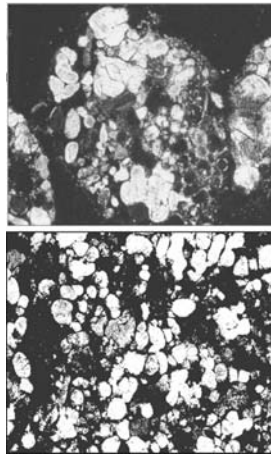


Fig. 2 Characteristic LOM photographs of solidified slag sample

Besides the qualitative mineralogical analysis, based on the results of the XRD analysis, approximated quantitative mineralogical compositions of the samples were produced. The results are presented in Table 2.

The dominant amount of γ -modification of dicalcium silicate (γ -2CaOSiO₂), which is product of polymorph transformation of β -dicalcium silicate in the process of slag cooling, was registered in all investigated samples. Considerable amount of periclase (MgO) was found in all investigated samples. Interferential reflections of minerals melilite and merwinite (Ca₃Mg(SiO₄)₂) were also identified. Melilite ((Ca,Na)₂(Al,Mg,Fe⁺)(Si,Al)₂O₇) was solid solution of gellenite (2CaOAl₂O₃SiO₂) and akermanite (Ca₂MgSi₂O₇). Very small amounts of the minerals rankinite (Ca₃Si₂O₇) and diopside (CaMgSi₂O₆) were noticed in the samples that were not heat-treated and in the samples that were heat-treated at 200°C.

Obtained results showed very small influence of the applied heat treatments to the mineral composition of the investigated slag samples.

The optical microscopy analysis was conducted in the purpose of more complete mineralogical analysis. Characteristic photographs of the investigated slag sample is shown in Fig. 2.

Characteristic crossed nicols γ -2CaOSiO₂ can be noticed in Fig. 2.

Microstructure analysis

Microstructure of slag with characteristic maps of elements distribution and line scans are given in further chapters. Microstructure of the slag sample with characteristic maps of distribution for: Ca, Mg, Si and Al is shown in Fig. 3.

Mapping and line scanning analysis of the investigated slag were in a good accordance with the results of mineralogical analysis. Maps of distribution

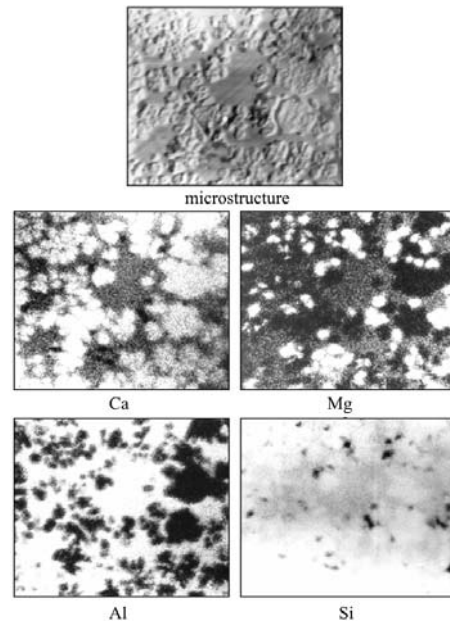


Fig. 3 Characteristic microstructure of slag with the elements distribution maps

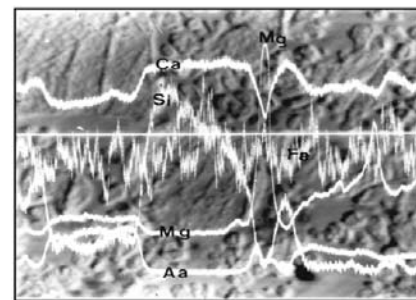


Fig. 4 Microstructure of the slag with the line scanning results

for magnesium and calcium were characterized by existence of number of regions with different concentrations of these elements. This is especially noticeable in the case of magnesium, which agreed well with the results of XRD analysis. The biggest amount of magnesium was in the form of periclase (MgO). Silicon was present along the entire microstructure surface. Map of aluminum distribution displayed the regions with very small amount of aluminum, which corresponded well to the regions with the smallest magnesium concentration.

Thermal analysis

The thermal microscopy results showed that heating of the slag to 810°C did not cause any changes in the samples dimensions. At 810°C slight contraction of the slag sample started and continued to 1450°C. At this temperature expansion of the sample dimensions started and at 1470°C sample started melting. Melting of the slag finished at 1480°C with the sample effusion.

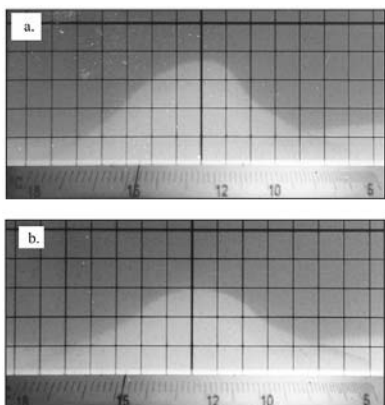


Fig. 5 Slag melting at: a – 1470°C and b – 1480°C

Beginning of melting and sample effusion is shown in Fig. 5.

In order to perform more detailed examination of slag behaviour in the heating process DTA and TG measurements were carried out. Characteristic DTA and TG curve is shown in Fig. 6.

The mass loss up to 740°C is product of sample dehydration. The low-temperature endotherm, with the peak temperature of 138.2°C, has been ascribed to loss of water from hydrated calcium silicate gels. This was followed by an endotherm occurrence at 324.5°C, due to decomposition of calcium hydroxide, which was formed by hydrolysis of some of the calcium silicates originally present. A third exothermic effect at 931°C was possibly associated with the reaction between the constitutive oxides but the precise justification was not determined in the present work.

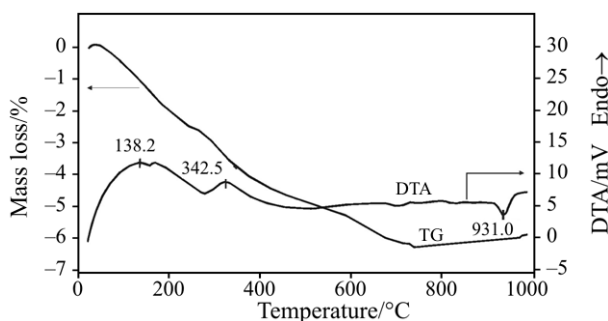


Fig. 6 DTA-TG curves of slag sample

Conclusions

The results of chemical analysis refer that slag of silicothermic reduction process can be approximately described as quaternary CaO–SiO₂–Al₂O₃–MgO system having in mind that these components form almost 96% of slag bulk.

Solidified slag contained following minerals: γ -2CaOSiO₂, periclase (MgO), melilite ((Ca,Na)₂(Al,Mg,Fe⁺⁺)(Si,Al)₂O₇), merwinite

(Ca₃Mg(SiO₄)₂), rankinite (Ca₃Si₂O₇) and diopside (CaMgSi₂O₆).

The biggest part of magnesium was in the form of periclase and merwinite.

Heating of the slag samples up to 800°C did not cause significant changes in the mineralogical composition of slag.

TG analysis showed mass loss during the heating process up to 740°C. This was due to sample residual moisture.

Based on the thermal microscopy analysis it can be concluded that from 810°C slight sample contraction was taking place while slag melted in the 1470–1480°C temperature interval.

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