

Laboratory technological research of magnesium intermediates preparation from the dolomites raw materials suitable for magnesium metal production

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Abstract: Metallic magnesium has been included in the list of Critical Mineral Raw Materials (CRM) for European Union countries since 2010. The territory of the Slovak Republic has large reserves of mineral raw materials – magnesite and dolomite, which are the initial source of metal Mg. For technological research, the following raw materials (based on chemical analyses of samples) were chosen: dolomite ore from the Sedlice deposit (SED-1), Trebejov deposit (TR-1) and dolomite ore from the Kraľovany deposit (KRA-1). The second deposit is also located near the operation of a potential customer of laboratory results for the production of metal magnesium, OFZ a.s. The aim of the laboratory technological research was to determine the experimental conditions for obtaining suitable Mg intermediates for metal magnesium preparation. For this purpose, there were performed DTA/TG and XRD analyses to study its behaviour, total mass loss and amount of carbon dioxide after calcination process. By optimizing the annealing tests of dolomite, products were obtained that met two conditions for its subsequent use in the sillicothermal process, namely the molecular ratio of CaO/MgO, content of impurities and the content of CO₂. The optimization of calcination and repeated annealing pointed at the suitable conditions of dolomite raw sample processing (temperature of 1 050 °C for 2.5 hours, or 1 100 °C for 2 hours).

Key words: dolomite, annealing, calcinated dolomite

Graphical abstract

DOLOMITE

Laboratory technological processing and detailed characterization

Optimization of annealing process, chemical, structural and thermal analyses

Calcinated dolomite – product for sillicothermal method of metal magnesium preparation

Highlights

- Domestic dolomite raw materials were technologically processed and characterized in detail.
- Calcinated dolomite samples exhibited changes of mineralogical phases, thermal and structural properties.
- Semi products prepared by optimization of annealing process possess the potentiality to be a suitable material for metal magnesium preparation.

1. Introduction

The topic of the availability of some metals or raw materials in the world, and especially in Europe, lasts for a decade. From 2010, when the first analysis of critical metals was prepared, further detailed analyses were elaborated, taking into account the greater need for the raw materials and their availability on world markets, as well as their cost. European countries remain a major importer of a large portion of metals and minerals, which are inevitable for the technologies used and for products necessary for economic growth and development. The European Commission has published the latest version of

the study of Critical Raw Materials for EU countries with position of individual metals and raw materials regarding the import risk and economic importance in 2015 (Report of EC, 2015). The share of domestic production, as well as the presence of verified, but also estimated sources of these raw materials in the EU countries, are very small or possibly none. For this reason, the countries of the European Union are dependent on import of such raw materials.

Magnesium is the eighth most abundant element in the Earth's crust and it is also extractable from brine and seawater. The sources and raw materials from which

magnesium could be produced include also camallite, dolomite, serpentine and magnesite (Ramakrishnan & Koltun, 2004). Magnesium has a density two-thirds that of aluminium, one-quarter that of steel and only slightly higher than that of many polymers (Chen et al., 2015). It is also recycled easily compared with polymers, which makes it environmentally friendly (Prado & Cepeda-Jimeréz, 2015). Because of the substantial magnesium resources and the attractive magnesium products, magnesium metal is regarded as a potentially ideal substitute for aluminum metal- but the global annual production of magnesium metal is only 1.8 % that of aluminum metal (Zhang et al., 2022).

Magnesium is produced commercially either by electrolyzing the magnesium chloride derived from raw materials, or by using a thermal reduction process, known as the Pidgeon process, using dolomite as the raw material. The process was invented and developed in Canada by Dr L. M. Pidgeon, in the early 1940s (Mehrabi et al., 2012), where a plant for magnesium production based on the ferrosilicon process was built to produce magnesium at the rate of ~4 500 kg per annum (or 10,000 lb per year) (Ramakrishnan & Koltun, 2004). The thermal reduction method is based on the chemical reduction between calcined dolomite ($\text{CaO} \cdot \text{MgO}$) and ferrosilicon (Si-Fe) at high temperature (1 100–1 250 °C) and high vacuum (1.33–13.3 Pa) (Zhang et al., 2022).

The territory of the Slovak Republic has large reserves of mineral raw materials – magnesite and dolomite, which are the initial source of metal Mg. The supplies of these raw materials in Slovakia are immense in comparison to other European countries.

The dolomites in Slovakia occur in several Middle and Upper Triassic formations thick up to several 100 meters, or forming intercalations, interbeds, lenses in beds irregularly alternating with surrounding limestones. They are present in numerous geological units, their cover sequences and tectonic nappes. The most significant are the Middle- and Upper-Triassic dolomites of the Hronic unit, bearing the important dolomite deposits in the Choč nappe of the Strážovské vrchy Mts. (Fig. 1).

There are known some experimental works on magnesium metal production from raw magnesite (Tomášek & Špet'uch, 1995; Tomášek et al., 1997). There were even considerations on running its production in the Slovak Magnesite Works in Jelšava (Immer, 1998). The positive results of the production of intermediate products from dolomites and magnesites have been obtained recently. The own laboratory experiment of the production of metallic magnesium by the silicothermal method was

carried out at the SGUDS, regional centre Košice. Under experimental conditions, it was possible to prepare separate reduced crystals of metallic magnesium (Bačo et al., 2016). The aim of this work is to prepare suitable intermediates for the Mg production by the calcination process with the molecular ratio of $\text{CaO} : \text{MgO}$ in the range of 1.1 to 1.5 (close to the composition of the dolomite raw materials), with the maximum impurity content 2.5 % ($\text{R}_2\text{O}_3 + \text{SiO}_2$) and CO_2 content below 0.3 %, otherwise the magnesium yield drops sharply (Tomášek et al., 1997). From a mixture of $\text{CaO} + \text{MgO}$ oxides in the above-mentioned ratio using ferrosilicon (FeSi75) and in the presence or absence of a catalyst (CaF_2) it is possible to prepare metallic Mg by silicothermal reduction by condensation of its vapours in a vacuum or in an inert atmosphere (due to its reverse oxidation to MgO at normal pressure) (Tuček et al., 2016).

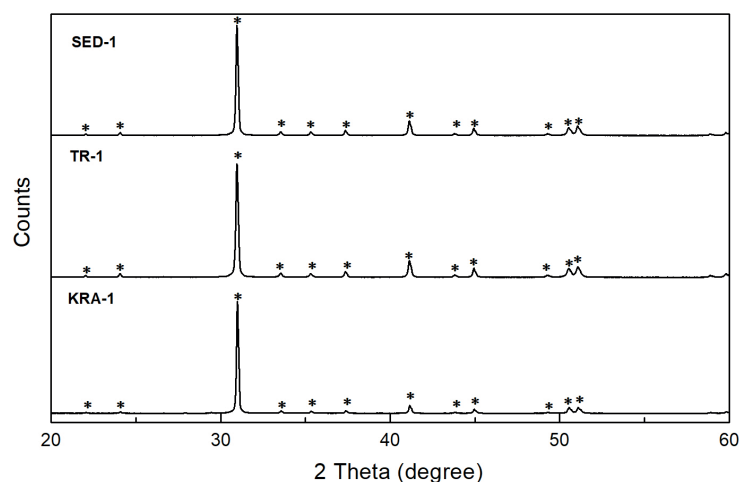


Fig. 1. Significant dolomite deposits in individual geological units of the Western Carpathians. Yellow pentagon and designations in bold in location indicate the deposits with reserves stated in the Balance of Reserves in Reserved Deposits with the state to 1. 1. 2018.

2. Materials and Methods

2.1. Raw materials

For experimental purposes, dolomite ores from the Sedlice (SED-1), Trebejov (TR-1) and Kral'ovany (KRA-1) deposits were chosen as raw materials. Bulk samples of dolomites were freely air-dried and subjected to preparatory work – crushing in three stages in jaw crushers and sorting on sieves of different sizes: + 8.0; 4.0 – 8.0; 2.0 – 4.0; 1.0 – 2.0; –1.0 mm; whereas all samples, or the grain fractions prepared from them were subsequently homogenized and quartered. From each raw sample after these works and from the grain size classes, individual homogeneous parts were prepared for further laboratory processing, including their grain size characteristics.

2.2. X-ray diffraction analyses

Qualitative mineralogical analysis of input samples was carried out by the X-ray diffraction (XRD) method on the BRUKER D2 Phaser device: $\text{CuK}\alpha$ radiation, monochromatic Ni filter, accelerating voltage of the X-ray radiation generator 30 kV, current intensity 10 mA, range of detected angles $5 - 70^\circ 2\theta$, step 0.01° , time 0.3 sec/step. Processing and evaluation of measured data were realized using the software DIFFRAC.EVA V3.1. Measurement, equipped with the PDF-2/2013 database.

2.3. Differential thermal analyses/Thermogravimetric analyses (DTA/TG)

NETZSCH STA 449 F3 Jupiter derivatograph (NETZSCH Gerätebau GmbH., Selb, Germany) equipped with a Std SiC furnace and an Autovac MF Cs rotary pump was used for thermal DTA/TG analysis. Measurements were made under the following conditions: heating range: $24 - 1\ 000^\circ\text{C}$, heating rate $10^\circ\text{C} \cdot \text{min}^{-1}$, reference material: powdered Al_2O_3 , crucibles: ceramic Al_2O_3 , furnace atmosphere: N_2 , N_2 circulation: $20\ \text{ml} \cdot \text{min}^{-1}$.

2.4. Annealing tests

Annealing tests of dolomite fractions were carried out in an electric laboratory furnace ELOP-1200/15 at temperatures of $1\ 000^\circ\text{C}$ and $1\ 050^\circ\text{C}$ with a holding time of 0.5; 1; 2 and 2.5 hours.

Input samples of raw materials and processed intermediates/products were subjected to chemical analysis using the Röntgenfluorescence energodispersion spectrometer (XRF) X-LAB 2000, Spectro in the Geoanalytical laboratories of the SGUDS in Spišská Nová Ves.

3. Results

3.1. Mineralogical and thermic analyses of raw dolomites

Dolomite raw materials were characterized by high purity, in the case of the SED-1 sample, the presence of the monomineral phase of dolomite was confirmed. In addition to a high proportion of dolomite, sample TR-1 also contained an accessory proportion of quartz and sample KRA-1 accessory proportion of calcite (Fig. 2).

Dolomite is a mineral with a calcite superstructure, formed by both magnesite and calcite molecules, $\text{CaMg}(\text{CO}_3)_2$. During thermal decomposition, MgCO_3 molecules are less stable and release CO_2 earlier than the CaCO_3 compound.

The mineralogical analysis of the SED-1 dolomite sample pointed to the high purity of the raw material, without the detection of any impurities. Two significant endothermic decreases can be observed from the DTA curve, where at a temperature of 793°C , CO_2 is released from MgCO_3 dolomite molecules and the corresponding weight loss represents 20.04 % of the sample weight. At a higher temperature, 852°C , CO_2 is released from CaCO_3 molecules and this decomposition corresponds to a mass loss of 25.78 %. The total weight loss in the temperature range of $700 - 900^\circ\text{C}$ is 45.82 % and corresponds to the decomposition of dolomite (Fig. 3).

The composition of dolomite sample TR-1 is also characterized by high purity, with minimal participation of quartz admixture. DTA analysis of the sample has a characteristic curve for dolomite with two significant

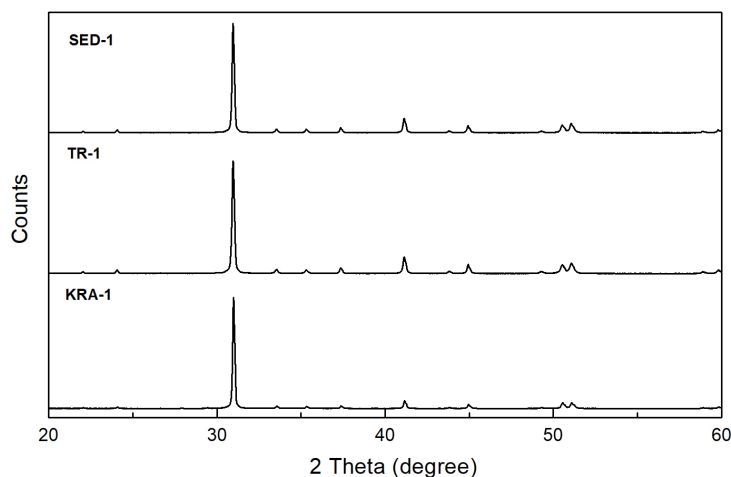


Fig. 2. XRD analyses of raw samples SED-1, TR-1 and KRA-1 (* – dolomite).

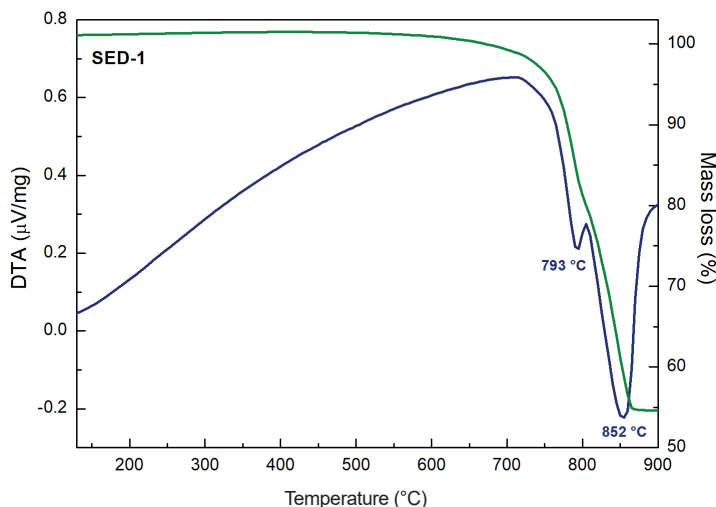


Fig. 3. DTA/TG analysis of raw sample SED-1.

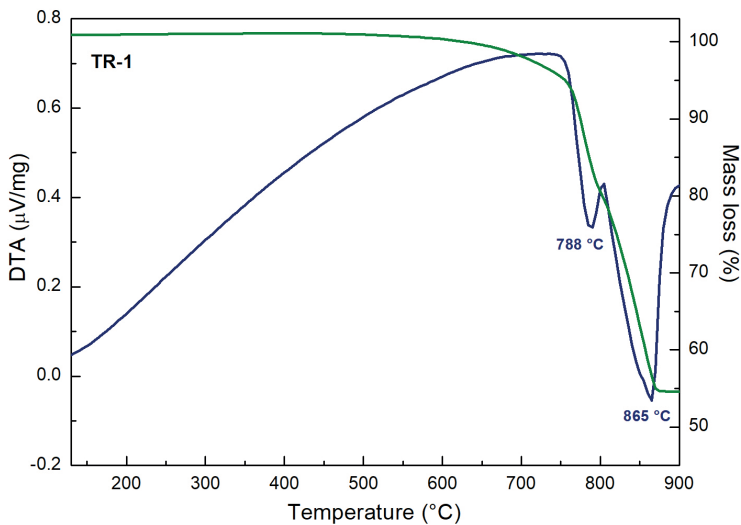


Fig. 4. DTA/TG analysis of raw sample TR-1.

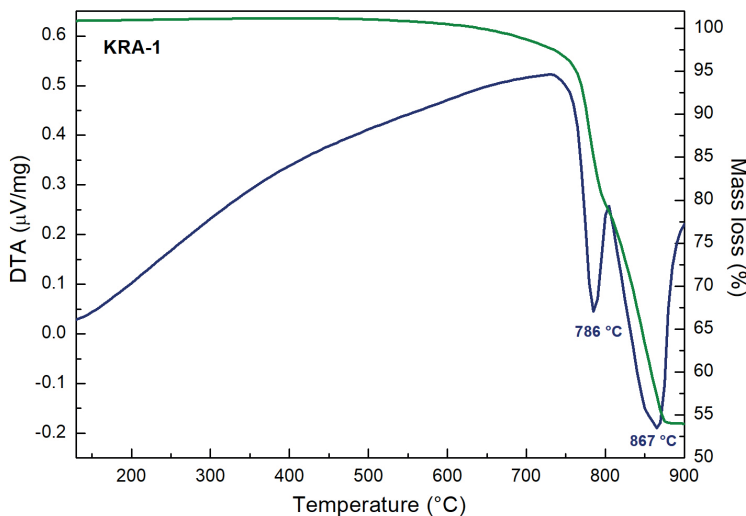


Fig. 5. DTA/TG analysis of raw sample KRA-1.

endothermic reactions at temperatures of 788 °C and 865 °C. The total weight loss represents 45.85 %, while the release of CO_2 from the decomposition of MgCO_3 of dolomite molecules corresponds to 20.11%, the CO_2 coming from the decomposition of CaCO_3 is 25.74 % of the sample weight (Fig. 4).

For the sample KRA-1 two endothermic decreases were observed at temperatures of 786 °C and 867 °C corresponding to weight loss of 20.32 % and 25.91 %, respectively (Fig. 5).

3.2. Chemical analyses

The separated and homogenized fractions of dolomite raw materials were subjected to chemical analysis for further laboratory processing. The results of chemical

analyses of separated grain size classes are shown in Tab. 1.

3.2. Results of annealing tests of dolomite raw materials

Separated grain size fractions of the tested dolomite ores were evaluated after annealing tests in terms of annealing loss (Tab. 2).

From the Tab. 2 it can be observed that for the SED-1 sample, the required thermal decomposition (above 98 %) occurs in the coarse-grained fraction (4 – 8 mm) at both temperatures, regardless of the annealing time. On the contrary, the fraction below 1 mm is the most stable and the required dolomite decomposition occurs after annealing at 1 050 °C for more than 2 hours. For this sample, annealing of grain fractions above 1 mm was effective at the temperature of 1 050 °C with a holding time of minimal 0.5 hours.

For sample TR-1, only annealing of fractions over 2 mm at the temperature of 1 050 °C with a duration of over 2 hours was effective. On the contrary, the sample KRA-1 reached required decomposition for all studied grain fractions at both temperatures.

After initial annealing tests, optimization of the process was carried out. Individual fractions of all samples were combined and annealed at temperatures of 1 050 °C for 2.5 hours and 1 100 °C for 1 hour. The products after annealing and chemical analysis were evaluated with regard to the required conditions for calcined dolomite. The preparation of the product from the dolomite raw material into the mixture for the batch for the silicothermal production of Mg consists in the preparation

of calcined dolomite ($\text{CaO} \cdot \text{MgO}$) so that the molecular ratio of $\text{CaO} : \text{MgO}$ is in the range of 1.1 to 1.5 : 1, the content of impurities together with SiO_2 is below 2.5 % and a maximum CO_2 content of 0.3 % (Blahút et al., 1994).

Products from input ore samples SED-1, TR-1 and KRA-1, annealed at both selected temperatures, met two of the three conditions, namely the molecular ratio of $\text{CaO} : \text{MgO}$ and the content of impurities below 2.5 %. The SED-1 sample after the optimized annealing process showed a CO_2 content of 0.37 % (for $t = 1\ 050\ ^\circ\text{C}$) and 0.44 % (for $t = 1\ 100\ ^\circ\text{C}$), the TR-1 sample had contents of 0.33 % and 0.51 %, and KRA-1 0.40 and 0.44 %, respectively (Tab. 3).

The samples after calcination (1 050 °C/2.5 hours) were characterized by the X-ray diffraction and DTA/TG analyses with the aim to describe the structural changes

Tab. 1 Basic chemical composition of particular grain fractions of dolomite ore samples SED-1, TR-1 and KRA-1

Sample	Fraction [mm]	Mass yield [%]	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	TiO ₂	MnO	K ₂ O Na ₂ O [%]	P ₂ O ₅	Chemical composition S _{tot} , SO ₃ , FeO	CO ₂	A. I.	Hg	Sb	C	Ni As [mg/kg]	Pb	Cd	Sr	
SED-1	input	100	1.07	0.16	0.20	30.3	20.9	<0.01	0.01	<0.005	<0.001	<0.05	46.7	47.3	0.10	<2	<5	<4	<5	<1	<1	79
	4-8	57.77	0.44	0.16	0.12	30.4	21.3	<0.01	<0.01	<0.005	<0.001	0.10	42.8	47.3	<0.01	<2	<5	<4	<5	<1	<1	71
	2-4	25.31	0.28	0.15	0.11	30.4	21.3	<0.01	<0.01	<0.005	<0.001	0.05	41.4	47.5	<0.01	<2	<5	<4	<5	<1	<1	73
	1-2	7.02	0.38	0.16	0.10	30.3	21.3	<0.01	<0.01	<0.005	<0.001	0.08	42.8	47.6	<0.01	<2	<5	<4	<5	<1	<1	72
TR-1	-1	9.90	0.44	0.19	0.26	30.4	21.2	<0.01	0.01	<0.005	<0.001	0.08	41.4	47.3	0.03	<2	<5	22	11	<1	<1	72
	input	100	1.02	0.42	0.24	30.4	21	0.02	<0.01	0.05	0.01	0.05	46.8	46.8	<0.01	<2	<5	5	<5	<1	<1	72
	4-8	55.4	1.37	0.45	0.28	30	20.8	0.02	0.01	0.16	0.01	0.18	42.1	46.7	<0.01	<2	<5	<4	<5	<1	<1	68
	2-4	24.4	1.06	0.40	0.25	30.1	21	0.02	0.01	0.13	0.01	0.08	42.5	46.9	<0.01	<2	<5	<4	<5	<1	<1	68
KRA-1	1-2	8.13	0.92	0.41	0.23	30	21	0.02	0.01	0.15	0.01	0.10	41	47.2	<0.01	<2	<5	<4	<5	<1	<1	67
	-1	12.1	1.25	0.45	0.27	29.9	20.9	0.02	0.01	0.11	0.01	0.13	41	46.8	0.01	<2	5	21	<5	<1	<1	67
	input	100	0.12	<0.05	<0.05	30.6	21.4	<0.01	<0.01	<0.005	<0.001	<0.05	46.6	47.7	<0.01	<2	<5	<4	<5	<1	<1	46
	4-8	51	<0.05	<0.05	<0.05	30.4	21.4	<0.01	<0.01	<0.005	<0.001	0.33	43.2	47.7	<0.01	<2	<5	<4	<5	<1	<1	46
	2-4	30.4	<0.05	0.08	0.07	30.5	21.3	<0.01	<0.01	<0.005	<0.001	0.10	43.2	47.8	<0.01	<2	<5	<4	<5	<1	<1	47
	1-2	8.36	<0.05	<0.05	<0.05	30.7	21.4	<0.01	<0.01	<0.005	<0.001	<0.05	42.1	47.8	<0.01	<2	<5	<4	<5	<1	<1	47
	-1	10.3	0.07	<0.05	<0.05	31.3	21	<0.01	<0.01	<0.005	<0.001	0.05	43.2	47.5	<0.01	v2	<5	9	<5	<1	<1	45

A. I. – annealing loss

Tab. 2

Annealing loss depending on grain fractions, temperature and heating period for dolomite samples SED-1, TR-1 and KRA-1

Sample	SED-1 (Sedlice)							
Temperature	1 000 °C				1 050 °C			
Time	0.5 h	1.0 h	2.0 h	2.5 h	0.5 h	1.0 h	2.0 h	2.5 h
Fraction [mm]	Annealing loss [%]							
4–8	46.85	46.89	47.15	46.90	47.16	47.09	47.24	47.10
2–4	46.72	46.92	47.08	46.79	46.91	46.97	47.20	47.10
1–2	46.70	46.75	46.99	46.92	46.96	46.96	47.10	47.01
Below 1	46.30	46.34	46.69	46.46	46.66	46.73	46.89	46.84
	Theoretical dolomite decomposition to loss by annealing [%]							
4–8	98.16	98.24	98.78	98.26	98.81	98.66	98.97	98.68
2–4	97.88	98.30	98.64	98.03	98.28	98.41	98.89	98.68
1–2	97.84	97.95	98.45	98.30	98.39	98.39	98.68	98.49
Below 1	97.00	97.09	97.82	97.34	97.76	97.90	98.24	98.14
Sample	TR-1 (Trebejov)							
Temperature	1 000 °C				1 050 °C			
Time	0.5 h	1.0 h	2.0 h	2.5 h	0.5 h	1.0 h	2.0 h	2.5 h
Fraction [mm]	Annealing loss [%]							
4–8	46.31	46.32	46.71	46.66	46.48	46.56	46.79	46.91
2–4	46.24	46.38	46.55	46.67	46.47	46.47	46.73	46.88
1–2	46.10	46.19	46.32	46.44	46.27	46.40	46.69	46.73
Below 1	45.75	45.80	46.07	46.17	45.87	46.09	46.55	46.59
	Theoretical dolomite decomposition to loss by annealing [%]							
4–8	97.02	97.05	97.86	97.76	97.38	97.55	98.03	98.28
2–4	96.88	97.17	97.53	97.78	97.36	97.36	97.90	98.22
1–2	96.58	96.77	97.05	97.30	96.94	97.21	97.82	97.90
Below 1	95.85	95.96	96.52	96.73	96.10	96.56	97.53	97.61
Sample	KRA-1 (Kraľovany)							
Temperature	1 000 °C				1 050 °C			
Time	0.5 h	1.0 h	2.0 h	2.5 h	0.5 h	1.0 h	2.0 h	2.5 h
Fraction [mm]	Annealing loss [%]							
4–8	47.36	47.35	47.38	47.33	47.36	47.47	47.47	47.40
2–4	47.29	47.30	47.30	47.26	47.30	47.41	47.37	47.34
1–2	47.19	47.30	47.31	47.22	47.28	47.33	47.37	47.29
Below 1	46.94	47.08	47.04	47.00	47.01	47.21	47.16	47.11
	Theoretical dolomite decomposition to loss by annealing [%]							
4–8	99.22	99.20	99.27	99.16	99.22	99.46	99.46	99.31
2–4	99.08	99.10	99.10	99.02	99.10	99.33	99.25	99.18
1–2	98.87	99.10	99.12	98.93	99.06	99.16	99.25	99.08
Below 1	98.34	98.64	98.55	98.47	98.49	98.91	98.81	98.70

Tab. 3
Products of calcination of crushed dolomite SED-1, TR-1 and KRA-1 below 8 mm

SED-1 (Sedlice)													
Sample Conditions of calcination	Chemical composition [%]												
	CaO	MgO	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	Na ₂ O	K ₂ O	P ₂ O ₅	CO ₂	CaO : MgO	Σ R ₂ O ₃
1 050 °C; 2.5 hrs	30,60	21,70	0,24	<0,01	0,15	0,10	<0,01	<0,2	<0,05	<0,01	0,37	1,41	0,86
Chemical composition [%]													
calcination	CaO	MgO	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	Na ₂ O	K ₂ O	P ₂ O ₅	CO ₂	CaO : MgO	Σ R ₂ O ₃
1 100 °C; 1 hr	30,60	21,70	0,21	<0,01	0,14	0,07	<0,01	<0,2	<0,05	<0,01	0,44	1,41	0,86
TR-1 (Trebejov)													
Chemical composition [%]													
calcination	CaO	MgO	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	Na ₂ O	K ₂ O	P ₂ O ₅	CO ₂	CaO : MgO	Σ R ₂ O ₃
1 050 °C; 2.5 hrs	30,10	21,30	1,02	0,02	0,47	0,21	<0,01	<0,2	<0,05	0,01	0,33	1,41	2,06
Chemical composition [%]													
calcination	CaO	MgO	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	Na ₂ O	K ₂ O	P ₂ O ₅	CO ₂	CaO : MgO	Σ R ₂ O ₃
1 100 °C; 1 hr	30,10	21,30	0,88	0,02	0,41	0,23	<0,01	<0,2	<0,05	0,01	0,51	1,41	2,06
KRA-1 (Kraľovany)													
Chemical composition [%]													
calcination	CaO	MgO	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	Na ₂ O	K ₂ O	P ₂ O ₅	CO ₂	CaO : MgO	Σ R ₂ O ₃
1 050 °C; 2.5 hrs	30,70	21,60	<0,05	<0,01	<0,05	<0,05	<0,01	<0,2	<0,05	0,01	0,44	1,42	0,45
Chemical composition [%]													
calcination	CaO	MgO	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	Na ₂ O	K ₂ O	P ₂ O ₅	CO ₂	CaO : MgO	Σ R ₂ O ₃
1 100 °C; 1 hr	30,80	21,70	<0,05	<0,01	<0,05	<0,05	<0,01	<0,2	<0,05	<0,01	0,40	1,42	0,40

and changes of their thermal properties. The dolomite sample SED-1 after calcination showed two endothermic peaks on the DTA curve. Smaller one at a temperature of about 453 °C and more expressive at a temperature of 819 °C. The total weight loss for the SED-1 sample was 30 % (Fig. 6). A small endothermic peak at a temperature of 452 °C, probably corresponding to brucite MgOH_2 (thermal reaction of brucite appear at 350 – 450 °C), and a more expressive one at a temperature of 821 °C, corresponding to calcite, were also observed for the TR-1 sample. The total weight loss was about 28 % (Fig. 7). For the sample KRA-1 the first endothermic peak was appeared at about temperature 374 °C and the second one at 835 °C (Fig. 8). The total weight loss was 33 %. Difference between the theoretical weight loss and the mass loss on TG curve is not significant, is up to 1,5 % which can be caused by measurement or instrument deviation. The weight losses for samples TR-1, SED-1 and KRA-1 remained approximately constant.

Further experiments are planned to investigate differences in the calcination behaviour of dolomite samples, and in industrial use must be taken into account to ensure complete calcination according to selected temperatures.

The major mineralogical phases in all calcinated samples were calcite and periclase (Figs. 9 – 11). For samples SED-1 and TR-1, expressive content of vaterite and minor content of portlandite were also observed. In the samples SED-1 and KRA-1 the accessory proportion of aragonite was detected, too.

The presence of portlandite in the annealed samples is not desirable and is probably related to the analyzed higher content of CO_2 .

The samples after annealing showed a typical calcite structure. The surface of the calcinated samples was rougher compared to the raw samples, with significant smaller agglomerated calcite particles (Fig. 12).

The reason of higher CO_2 contents in the prepared products could be caused by the manipulation of the samples. The reaction of calcinated samples with airy CO_2 is very fast and it can occur also during the preparation of samples for chemical analyses. The chemical analyses were crucial for further optimization of dolomite processing. They are also time-consuming to process. In addition, the analyses can be performed only in the other workplace than raw material processing were realized. From this reason the DTA/TG and XRD analyses presented above were made on samples that had been freely standing for a certain time

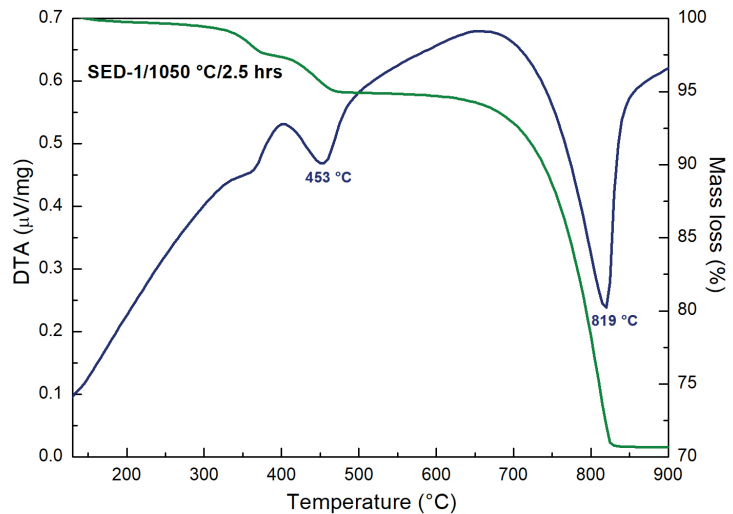


Fig. 6. DTA/TG analysis of calcinated sample SED-1; 1 050 °C/2.5 hours.

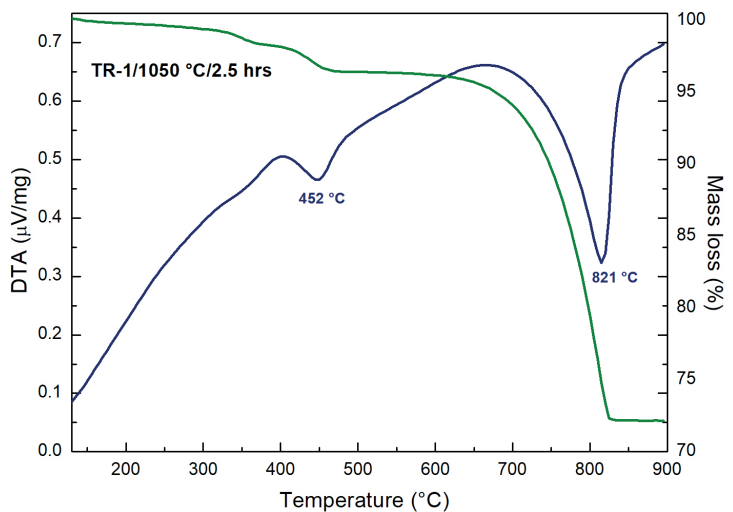


Fig. 7. DTA/TG analysis of calcinated sample TR-1; 1 050 °C/2.5 hours.

since calcination. On the basis of all obtained results, the control annealing and characterization were performed using only the DTA/TG and XRD analyses.

In order to exclude errors during the annealing process the raw dolomite samples were first annealed at higher temperature 1 100 °C for 2 hours. The thermogravimetric analyses were performed immediately. Almost non weight loss was observed for all studied samples, what pointed at the required decomposition of CaCO_3 (Figs. 13 – 15).

Also a control annealing of the KRA-1 sample at 1 050 °C for 2.5 hours was repeated. The sample was immediately characterized by X-ray diffraction measurement. The analysis showed total dolomite decomposition to required CaO and MgO compounds (Fig. 16).

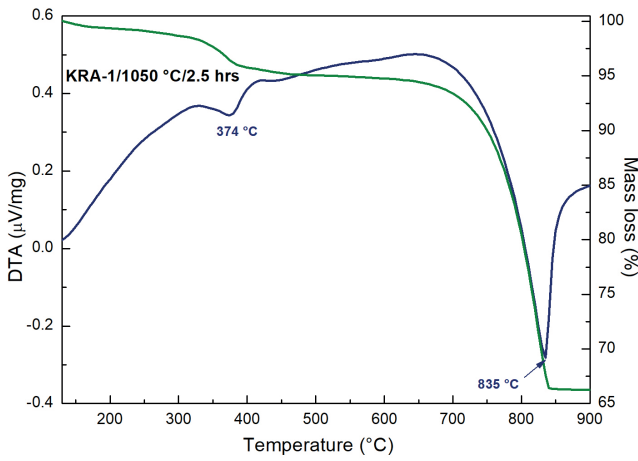


Fig. 8. DTA/TG analysis of calcinated sample KRA-1; 1 050 °C/2.5 hours.

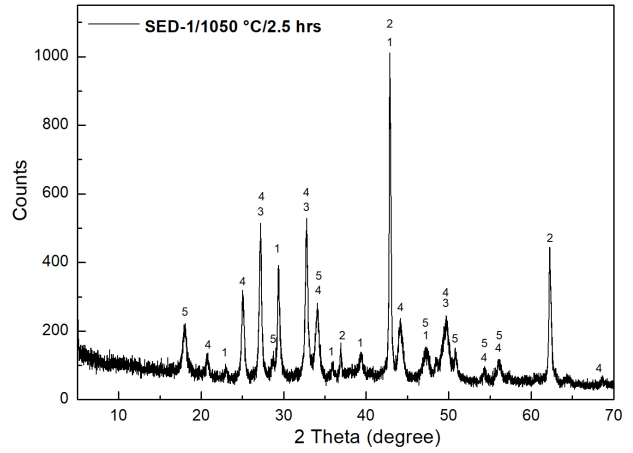


Fig. 9. XRD analysis of calcinated sample SED-1 (1 050 °C/2.5 hrs); 1 – calcite, 2 – periclase, 3 – aragonite, 4 – vaterite, 5 – portlandite.

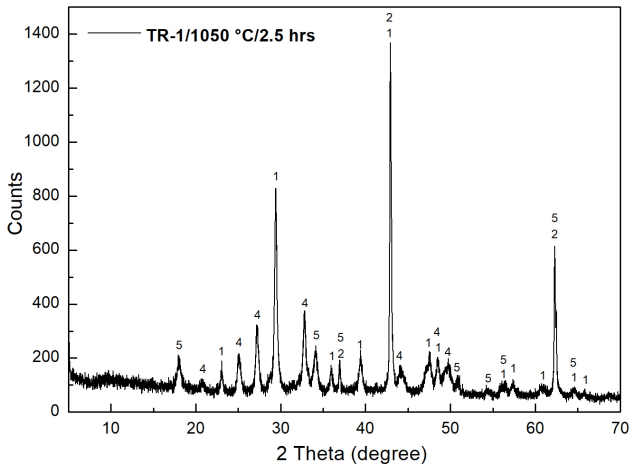


Fig. 10. XRD analysis of calcinated sample TR-1 (1 050 °C/2.5 hrs); 1 – calcite, 2 – periclase, 4 – vaterite, 5 – portlandite.

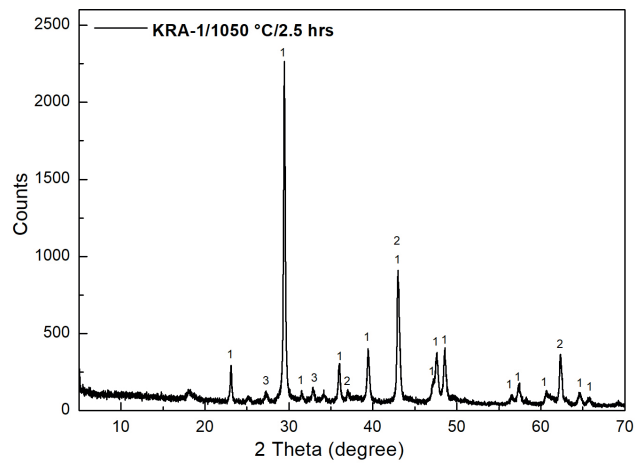


Fig. 11. XRD analysis of calcinated sample KRA-1 (1 050 °C/2.5 hrs); 1 – calcite, 2 – periclase, 3 – aragonite.

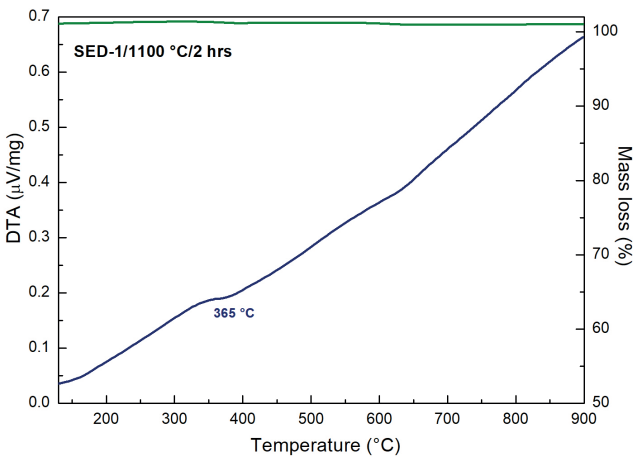


Fig. 13. DTA/TG analysis of calcinated sample SED-1; 1 100 °C/2 hours.

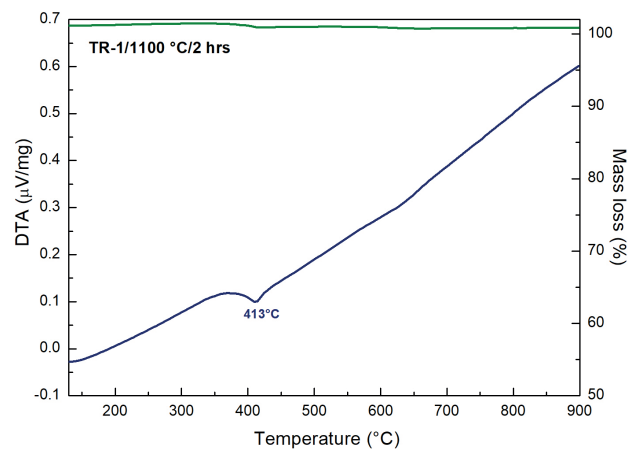


Fig. 14. DTA/TG analysis of calcinated sample TR-1; 1 100 °C/2 hours.

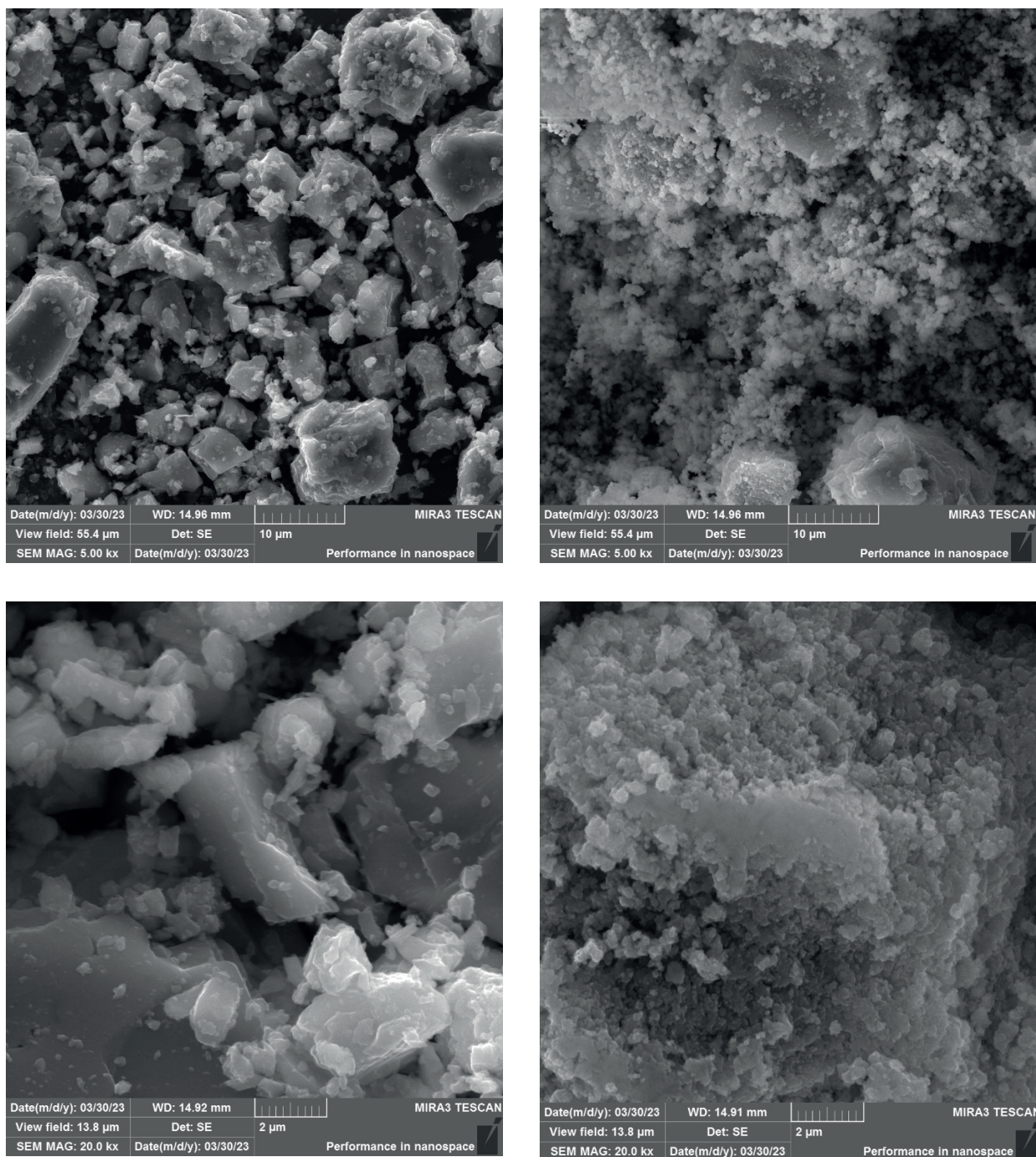


Fig. 12. Morphology of raw sample TR-1 (left up), TR-1 sample calcinated at 1 050 °C/2 hours (right up) and raw sample KRA-1 (left down), KRA-1 sample calcinated at 1 050 °C/2 hours (right down) observed by scanning electron microscope.

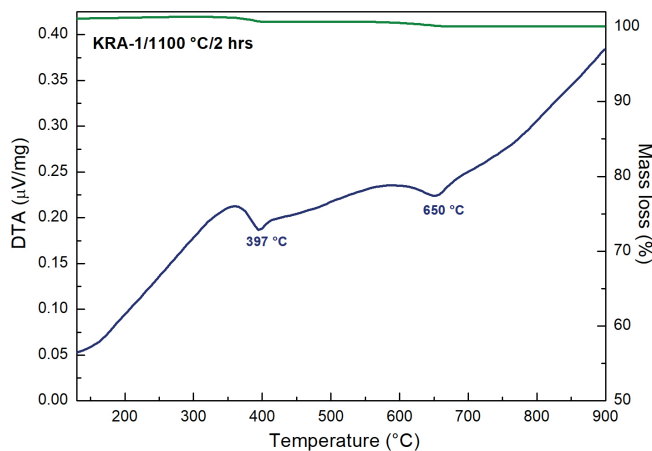


Fig. 15. DTA/TG analysis of calcinated sample KRA-1; 1 100 °C/2 hours.

The optimization of calcination and repeated annealing pointed at the suitable conditions of dolomite raw sample processing (temperature of 1 050 °C for 2.5 hours, or 1 100 °C for 2 hours) for magnesium metal production. The problematic are samples processing for chemical analyses, where the reaction with airy CO₂ should be prevented during the samples manipulation.

4. Conclusion

The aim of the study was the initial laboratory technological processing of selected domestic dolomite ores and their characterization. By annealing dolomites, according to chemical analyses, it is possible to obtain products that meet two conditions for their subsequent use as feedstocks in the silicothermal process for the preparation of metallic magnesium, namely the molecular ratio and the content of impurities. Control annealing of raw samples and their immediate characterization using DTA/TG and XRD pointed to the desired decomposition of dolomite, where the CO₂ content in the products should be at the required values. Furthermore, the conditions of chemical analyses of annealed samples will be studied in order to minimize the reaction of calcinated dolomites with atmospheric CO₂, which should be a suitable complement to structural and thermogravimetric analyses.

The knowledge obtained so far from the technological processing of dolomites will enable the development and testing of methods for the preparation of magnesium intermediates for semi-operational to operational conditions of their preparation. Given the current crisis situation caused by the lack of critical raw materials, the mentioned laboratory technological research is important also from the point of view of the use of high-quality domestic raw material resources, which can be interesting

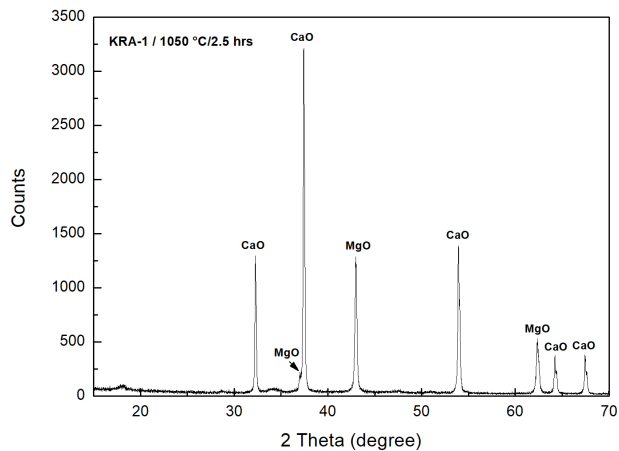


Fig. 16. XRD analysis of control calcination of sample KRA-1; 1 050 °C/2.5 hours.

and beneficial especially for manufacturers operating in the Slovak Republic.

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References

- BAČO, P., TUČEK, L., BAČOVÁ, Z., Čechovská, K., NÉMETH, Z., KOŠÚTH, M., KOVANIČOVÁ, L. & REPČIAK, M., 2016: Potential sources of raw materials for the production of magnesium metal. Final report of Geological task No. 15 13. *Manuscript. Bratislava, archive St. Geol. Inst. D. Štúr (in Slovak)*.
- BAČO, P., BROSKA, I., KOLLOVÁ, Z. & NÉMETH, Z., 2022: Inventory of critical raw materials in Slovakia. In: Critical raw materials in the economies of the V4 countries. *Katowice, Glow. Inst. Górn., 61–77*.
- BLAHÚT, I., RABATIN, L., TOMÁŠEK, K. & KOCÚR, J., 1994: Possibilities for the production of metal magnesium from dolomites and waste magnesite raw materials. *Uhlí a Rudy – Geol. Průzk., 6, 207–210 (in Slovak)*.
- CHEN, L.-Y., XU, J.-Q., CHOI, H., POZUELO, M., MA, X., BHOWMICK, S., YANG, J.-M., MATHAUDHU, S. & LI, X.-CH., 2015: Processing and properties of magnesium containing a dense uniform dispersion of nanoparticles. *Nature, 528, 539–543*.
- IMMER, J., 1998: Slovak magnesite plants Jelšava are increasing the export their products. *Týžd. Trend (in Slovak)*.
- MEHRABI, B., ABDELLATIF, M. & MASOUDI, F., 2012: Evaluation of Zefreh dolomite (central Iran) for production of magnesium via the Pidgeon process. *Min. Proc. Ext. Met. Rev., 33, 316–326*.

- PEREZ PRADO, M. T. & CEPEDA-JIMENEZ, C. M., 2015: Strength ceiling smashed for light metals. *Nature*, 528, 486–487.
- RAMAKRISHNAN, S. & KOLTUN, P., 2004: Global warming impact of the magnesium produced in China using the Pidgeon process. *Res. Conserv. Rec.* 42, 49–64.
- REPORT ON CRITICAL RAW MATERIALS FOR THE EU, 2015: Report of the Ad hoc Working Group on defining critical raw materials. *Ref. Ares (2015)1819503 – 29/04/2015, 41 pp.*
- TOMÁŠEK, K., RABATÍN, R., ŠPEŤUCH, V., ŠEŠEVIČKA, O., URBAN, E. & SITÁK, R., 1997: Patent Certificate Nr. 281 685: The method of production of magnesium from magnesite raw materials. 09 July 1997 (in Slovak).
- TOMÁŠEK, K. & ŠPEŤUCH, V., 1995: Laboratory verification of conditions for silicothermal reduction of dolomite. *Uhlí a Rudy – Geol. Průzk.*, 6, 184–185 (in Slovak).
- TUČEK, L., ČECHOVSKÁ, K., KOVANIČOVÁ, L., KOŠUTH, M. & MARČEKOVÁ, M., 2016: Potential sources of raw materials for the production of magnesium metal, Appendix No.1 – Technological part of Final report of Geological task No. 15 13, p. 9–10. *Manuscript. Bratislava, archive St. Geol. Inst. D. Štúr (in Slovak).*
- ZHANG, Z., LU, X. & YAN, Y., 2022: A novel pathway for the preparation of Mg metal from magnesia. *J. Magnes. Alloy*, 10, 2847–2856.

Laboratórny technologický výskum prípravy medziproduktov z dolomitovej suroviny vhodných na výrobu kovového horčíka

Problematika dostupnosti niektorých kovov či surovín vo svete, a najmä v Európe, trvá už desaťročie. Od roku 2010, keď bola vypracovaná prvá analýza kritických kovov, boli vypracované ďalšie podrobné analýzy zohľadňujúce väčšiu spotrebu nerastných surovín a ich dostupnosť na svetových trhoch, ako aj ich cenu. Európske krajiny ostávajú významným dovozcom veľkej časti kovov a nerastov, ktoré sú nevyhnutné pri používaných technológiách a produktoch potrebných na ekonomický rast a rozvoj. Európska komisia zverejnila najnovšiu verziu štúdie *Kritické suroviny pre krajiny EÚ* s postavením jednotlivých kovov a surovín z hľadiska dovozného rizika a ekonomického významu v roku 2015 (Správa EK, 2015). Podiel domácej produkcie, ako aj prítomnosť overených, ale aj odhadovaných zdrojov týchto nerastných surovín v krajinách EÚ sú veľmi malé, prípadne žiadne. Preto sú krajiny Európskej únie závislé od dovozu týchto nerastných surovín.

Horčík je ôsmy najrozšírejší prvok zemskej kôry a je aj extrahovateľný zo soľanky a morskej vody. Zdroje a suroviny, z ktorých by sa horčík mohol vyrábať, zahŕňajú aj kamallit, dolomit, serpentín a magnezit (Ramakrishnan a Koltun, 2004). Vzhľadom na možné surovinové zdroje horčíka a možnosti jeho využitia sa kovový horčík považuje za potenciálne ideálnu náhradu za kovový hliník, ale celosvetová ročná produkcia kovového horčíka tvorí len 1,8 % produkcie hliníka (Zhang et al., 2022).

Horčík sa komerčne vyrába buď elektrolyzou chloridu horečnatého získaného z nerastných surovín, alebo pomocou procesu tepelnej redukcie, známeho ako Pidgeonov proces, s použitím dolomitovej suroviny. Tento

proces vyvinul v Kanade Dr. L. M. Pidgeon začiatkom štyridsiatych rokov minulého storočia (Mehrabi et al., 2012). Bol tam postavený aj závod na výrobu horčíka (Ramakrishnan a Koltun, 2004). Metóda tepelnej redukcie je založená na chemickej redukcii medzi kalcinovaným dolomitom (CaO . MgO) a ferosiliciom (Si-Fe) pri vysokej teplote (1 100 – 1 250 °C) a vysokom vákuu (1,33 – 13,3 Pa) (Zhang et al., 2022).

Územie Slovenskej republiky disponuje veľkými zásobami nerastných surovín – magnezity, serpentinity a dolomity, ktoré sú východiskovým zdrojom kovového Mg. V predchádzajúcich prácach sa tieto suroviny širšie hodnotili a skúmali z technologického hľadiska. Ako najvhodnejšie na prípravu kovového Mg sa javili dolomity (Bačo et al., 2016). Dolomity na Slovensku tvoria samostatné súvrstvia v strednom a vrchnom triase hrubé až niekoľko sto metrov alebo vystupujú ako vložky, polohy, šošovky alebo telesá, nepravidelne sa prelínajúce s okolitými vápencami. Sú zastúpené vo všetkých geologických jednotkách, tak v obalových sekvenciách, ako aj v tektonických príkrovoch. Najväčší význam majú stredno- až vrchnotriasové dolomity hronika. Významnejšie ložiská sa nachádzajú v chočskom príkrove v Strážovských vrchoch.

Laboratórny pokus výroby kovového horčíka silikotermickou metódou sa uskutočnil aj v ŠGÚDŠ, regionálnom centre Košice. V laboratórnych podmienkach sa podarilo pripraviť samostatné redukované kryštály kovového horčíka (Bačo et al., 2016).

Cieľom štúdie bolo prvotné laboratórne technologické spracovanie vybraných domácich dolomitových rúd a ich charakterizácia. Na experimentálne účely sa zvolili

ako vstupné suroviny dolomity z lokalít Sedlice (SED-1), Trebejov (TR-1) a Kraľovany (KRA-1). Kusové nerozpadavé vzorky dolomitov sa voľne presušili na vzduchu a podrobili prípravným prácam – zdobňovaniu drvením a triedeniu na frakcie: +8,0; 4,0 – 8,0; 2,0 – 4,0; 1,0 – 2,0; –1,0 mm. Žihacie skúšky jednotlivých frakcií dolomitov sa realizovali v elektrickej laboratórnej peci ELOP-1200/15 pri teplote 1 000 a 1 050 °C s časom výdrže 0,5; 1; 2 a 2,5 hod. Vstupné vzorky a produkty kalcinácie boli charakterizované pomocou chemických, röntgeno(rtg.)difrakčných, diferenciálnych termických a termogravimetrických (DTA/TG) analýz.

Na základe rtg. analýz dolomitová vzorka zo Sedlíc (SED-1) obsahovala len minerálnu fázu dolomit, kým vstupná vzorka z Trebejova (TR-1) akcesorický podiel kremeňa a vzorka z Kraľovian (KRA-1) akcesorický podiel kalcitu.

Jednotlivé frakcie po žihacích skúškach boli vyhodnotené z hľadiska straty žiháním. V prípade vzorky SED-1 dochádzalo k požadovanému tepelnému rozkladu (vyše 98 %) v hrubozrnnej frakcii (4 – 8 mm) pri oboch hodnotách teploty, bez ohľadu na čas žihania. Naopak, frakcia menšia ako 1 mm bola najstabilnejšia. Požadovaný rozklad dolomitu nastal až po žihaní pri 1 050 °C pri výdrži viac ako 2 hodiny. Pri tejto vzorke bolo efektívne žihanie frakcií väčších ako 1 mm pri teplote 1 050 °C s časom výdrže minimálne 0,5 hodiny.

Pri vzorke TR-1 bolo účinné iba žihanie frakcií väčších ako 2 mm pri teplote 1 050 °C s výdržou viac ako 2 hodiny. Naopak, vzorka KRA-1 dosiahla požadovaný rozklad pri všetkých študovaných frakciách a pri oboch vybraných hodnotách teploty.

Po počiatkových skúškach žihania sa vykonala optimalizácia procesu. Jednotlivé frakcie dolomitových vzoriek menších ako 8,0 mm boli zlúčené a žihané pri teplote 1 050 °C s výdržou 2,5 hodiny a 1 100 °C s výdržou 1 hodinu. Produkty po žihaní a chemickej analýze sa vyhodnotili s ohľadom na požadované podmienky pre kalcinovaný dolomit do vsádzky na silikotermickú prípravu kovového Mg.

Príprava produktu z dolomitovej suroviny do vsádzky na silikotermickú výrobu Mg spočíva v príprave kalcinovaného dolomitu (CaO · MgO) tak, aby molekulárny pomer CaO : MgO bol v rozmedzí 1,1 až 1,5 : 1, obsah nečistôt spolu s SiO₂ menej ako 2,5 % a obsah CO₂ maximálne 0,3 % (Blahút et al., 1994).

Produkty zo vstupných vzoriek žiháných pri oboch vybraných hodnotách teploty spĺňali dve z troch podmienok, a to molekulárny pomer CaO : MgO a obsah nečistôt menej ako 2,5 %.

Vzorka SED-1 po optimalizovanom žihacom procese vykazovala obsah CO₂ 0,37 % (pri t = 1 050 °C) a 0,44 % (pri t = 1 100 °C), vzorka TR-1 obsah 0,33 a 0,51 %. Röntgenodifrakčná analýza poukázala na prítomnosť kalcitu a periklasu, ale aj menších podielov portlanditu, vateritu a aragonitu v kalcinovaných vzorkách. Prítomnosť portlanditu v produktoch po kalcinácii nie je žiaduca a súvisí s vyšším obsahom CO₂ stanoveným chemickou analýzou.

Príčina vyššieho obsahu CO₂ v pripravovaných produktoch môže byť spôsobená aj manipuláciou so vzorkami. Reakcia kalcinovaných vzoriek so vzdušným CO₂ je veľmi rýchla a môže nastať aj pri príprave vzoriek na chemické analýzy (mletie vzorky, príprava tablety na prvkovú rtg. analýzu). Pretože chemické analýzy boli kľúčové pre ďalšie laboratórne technologické spracovanie dolomitových vzoriek, uvedené rtg. a DTA/TG analýzy produktov sa realizovali až po získaní výsledkov z chemických analýz, teda v dôsledku „státia“ mohla nastať aj čiastočná degradácia vzoriek. Navyše, realizácia chemických analýz je časovo náročná a je možné vykonávať ich len na pracovisku GAL SNV, teda nie v mieste technologickej úpravy dolomitov. Vykonalo sa teda niekoľko ďalších žihacích skúšok a kontrolných DTA/TG meraní bez chemických analýz a na základe získaných výsledkov sa realizovalo kontrolné žihanie a charakterizácia produktov len pomocou DTA/TG a rtg. difrakčných analýz.

Aby sa vylúčili chyby počas procesu žihania s cieľom získať požadovaný žiháný produkt, vstupné vzorky dolomitov so zrnitosťou menej ako 8,0 mm sa najskôr 2 hodiny žihali pri vyššej teplote, 1 100 °C. DTA/TG analýzy sa uskutočnili okamžite po vychladnutí vzorky. Pri všetkých študovaných vzorkách sa nepozoroval takmer žiadny úbytok hmotnosti, čo poukazovalo na požadovaný rozklad CaCO₃.

Zopakovalo sa aj žihanie vzorky KRA-1 pri teplote 1 050 °C s výdržou 2,5 hod. Okamžite po vychladnutí bol produkt charakterizovaný pomocou rtg. difrakčnej analýzy, ktorá potvrdila rozklad dolomitu na požadované minerálne fázy CaO a MgO.

Optimalizácia kalcinácie a opakovaného žihania overila vhodné podmienky spracovania dolomitovej suroviny (teplota 1 050 °C počas 2,5 hodiny, resp. 1 100 °C počas 2 hodín) na výrobu kovového horčíka. Problematickým sa javí spracovanie vzoriek na chemické analýzy, kde by sa malo pri manipulácii so vzorkami zabrániť reakcii so vzdušným CO₂. Ďalej sa teda budú študovať podmienky prípravy žiháných vzoriek na chemické analýzy s cieľom minimalizovať reakciu kalcinovaných dolomitov

s atmosférickým CO₂, ktoré sa budú kontrolovať a doplnia sa výsledkami štruktúrnych a termogravimetrických analýz.

Doteraz získané poznatky z technologického spracovania dolomitov umožnia vývoj a testovanie metód prípravy horčikových medziproduktov v poloprevádzkových až prevádzkových podmienkach ich prípravy. Vzhľadom na súčasnú krízovú situáciu spôsobenú nedostatkom kri-

tických surovín je uvedený laboratórny technologický výskum dôležitý aj z hľadiska využívania kvalitných domácich surovinových zdrojov, ktorý môže byť zaujímavý a prínosný najmä pre výrobcov pôsobiacich v Slovenskej republike.

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