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SLOVAK DOLOMITE AS A RAW MATERIAL SOURCE FOR METAL MAGNESIUM PRODUCTION

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ABSTRACT – In order to ensure within the EU, preferably, self-sufficiency, a stable supply of the essential mineral raw materials required for industry led to the establishment of the European Raw Materials Alliance (ERMA). One of the key objectives is access to sustainable raw materials, as well as support for exploration and mining of raw materials within the EU. Metallic magnesium has been included in the list of critical minerals for European Union countries since 2011. The most suitable raw material for the MgO production for method of silicothermic reduction is dolomite or magnesite, at which Slovak Republic has considerable resources of these carbonate raw materials. For technological research, six samples from different deposites were chosen. The samples were annealed at selected temperatures and characterized by differential thermal analyses. The results showed that for the silicothermic reduction of magnesium, it is necessary to individually verify the calcination conditions for each sample and determine the influence of the hydration activity/active sites in their structure to increase the reduction of magnesium.

Keywords: Dolomite, Calcination, Metal Magnesium.

INTRODUCTION

Magnesium is produced commercially either by electrolysing 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 [1]. At present, China is the largest producer and exporter of magnesium in the world, accounting for more than 85 % of the world's magnesium outputs [2, 3].

The magnesium metal has a special status between 26 elements and minerals defined as "critical raw materials for the EU" [4].

The dolomite in Slovakia occurs in several Middle and Upper Triassic formations thick up to several 100 metres, or forming intercalations, interbeds, lenses in beds irregularly alternating with surrounding limestones. They are present in numerous geological units,

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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 Strážovská Highlands.

The reduced crystals of magnesium were prepared under experimental conditions by Kollová et al. [5].

In this paper the dolomite samples originated from different Slovak deposits were annealed with the aim to prepare suitable intermediate products for further silicothermic reduction in flowing argon to define a suitable thermal treatment of dolomite for preparing of magnesium metal according to the Pidgeon process.

EXPERIMENTAL

Raw samples

For experimental purposes, dolomite raw samples from the Slovak localities: Sedlice (SED-1, SED-2), Trebejov (TR-1), Stráňavy (ST-1, ST-2) and Kraľovany (KRA-1) were used. 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.

Experimental procedures

Annealing tests of dolomite fractions were carried out in an electric laboratory furnace ELOP-1200/15 at temperatures of 1000 °C and 1050 °C with a holding time of 0.5; 1; 2 and 2.5 hours. Optimized annealing tests of samples of fraction below 8.0 mm were carried out in an electric laboratory furnace KSL1600X-A2 at temperatures of 1150, 1200 and 1300 °C with a duration of 1.5 hours.

The crucibles were placed in a muffle furnace and then the furnace was heated up continuously from room temperature to selected temperature (the heating rate was 10 °C/min) with selected holding time. The products of calcination obtained at different temperatures were taken out and stored in a desiccator before DTA/TG analyses were carried out.

Methods of characterization

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

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

were made under the following conditions: heating range: 297 – 1273 K, heating rate 10 °C/min, reference material: powdered Al_2O_3, crucibles: ceramic Al_2O_3, furnace atmosphere: N_2 circulation: 20 ml/min.

The morphology of the prepared intermediate products was studied by scanning electron microscopy FE MIRA 3 (Tescan, Czech Republic) equipped by XRD energy-dispersive (EDX) analyzer of chemical composition (Oxford Instruments).

RESULTS AND DISCUSSION

For the samples KRA-1 and ST-1, the required thermal decomposition (above 98 %) was reached for all studied grain fractions at both temperatures (1000 and 1050 °C), as well as for the sample ST-2 except the fraction below 1.0 mm annealed at 1050 °C for 0.5 hour. For the samples SED-1 and SED-2 the decomposition occurs in the coarse-grained fraction (4-8 mm) at both temperatures with holding time of minimal 2 hours.
For sample TR-1, only annealing of fractions over 2 mm at the temperature of 1050 °C with a holding time of over 2 hours was effective [6].

After initial annealing tests, optimization of the process was carried out. Individual fractions of all samples were combined and annealed at temperatures at 1150, 1200 and 1300 °C for 1.5 hours in order to determine the appropriate temperature for the thermal decomposition of the investigated samples with respect to the theoretical loss by annealing. For samples SED-1, SED-2, TR-1 and KRA-1, the required thermal decomposition (above 98 %) occurred at temperatures of 1150 and 1200 °C. For samples ST-1 and ST-2, the required decomposition occurred only at a temperature of 1200 °C, Tab. 1.

Table 1 Parameters of calcined dolomites after annealing at selected temperatures

Temperature (°C)	Time (hrs)	Sample											
		SED-1		SED-2		TR-1		ST-1		ST-2		KRA-1	
		Annealing loss (%)	TD* (%)	Annealing loss (%)	TD (%)	Annealing loss (%)	TD (%)	Annealing loss (%)	TD (%)	Annealing loss (%)	TD (%)	Annealing loss (%)	TD (%)
1150	1.5	46.94	98.34	46.92	98.30	46.89	98.24	46.70	97.84	46.64	97.72	47.09	98.66
1200	1.5	47.11	98.70	47.22	98.93	47.01	98.49	46.98	98.43	47.02	98.51	47.01	98.49
1300	1.5	44.38	92.98	44.02	92.23	42.40	88.83	44.32	92.86	44.52	93.27	43.76	91.68

*TD - theoretical decomposition of dolomite to loss of annealing

In spite the shape of the DTA curves for each sample annealed at different temperatures was similar, Fig. 1, the most optimal annealing losses were achieved, except for the sample KRA-1, at a temperature of 1200 °C with a holding time of 1.5 hours. The annealing temperature of 1300 °C was already unsatisfactory for all samples. Low annealing loss values were determined for individual samples, probably due to reverse chemical reactions, but this was demonstrated on the DTA recording of the samples by only a weak hint of a peak at a temperature of around 400 °C for all the examined samples and another peak at a temperature above 600 °C for the ST-1 and KRA-1 samples (not shown here).

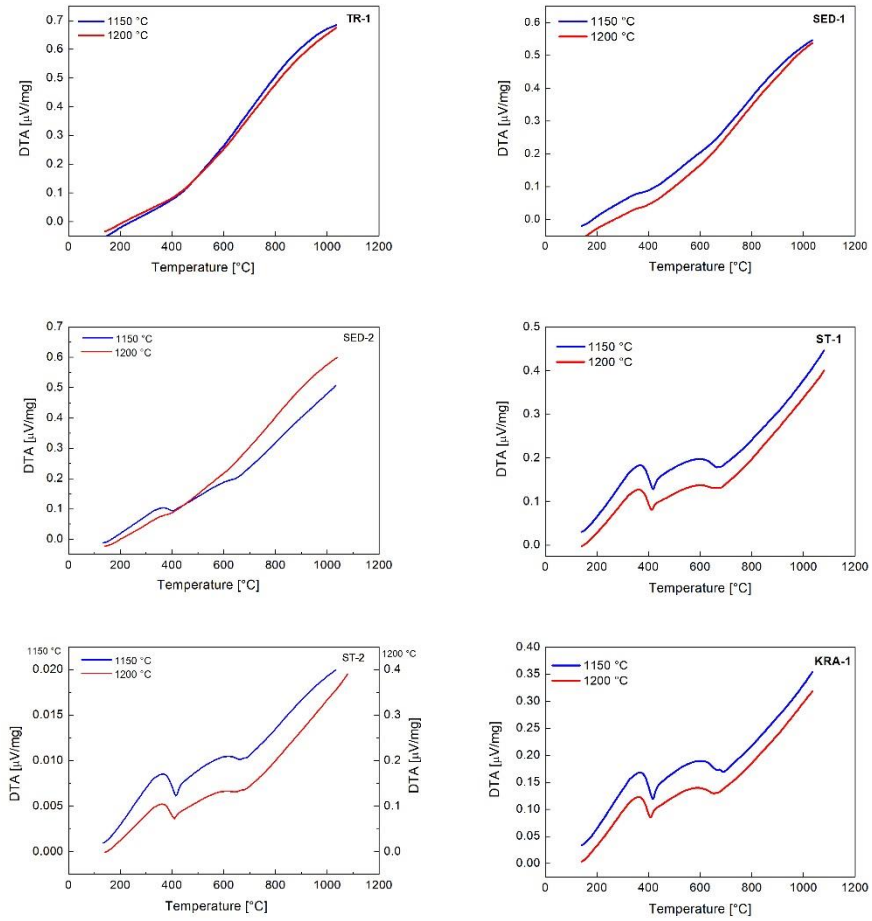

Figure 1 Comparison of DTA records of selected dolomite samples annealed at temperatures of 1150 °C and 1200 °C for 1.5 hours

Selected samples of dolomites (TR-1, SED-1, ST-1, KRA-1) annealed at temperature 1150 °C with holding time of 1.5 hours were subjected to repeated DTA/TG analysis after two months of "standing" in order to determine the degree of hydration of the samples, or stability of the prepared intermediates. The above analyzes resulted in the average weight loss for sample TR-1: 0.34 %, SED-1: 0.59 %, ST-1: 1.55 % and sample KRA-1: 1.54 %. In the dolomite sample, after repeated DTA/TG analysis after two months of "standing," the small agglomerated particles of dolomitic lime were observed on its surface, Fig. 2.

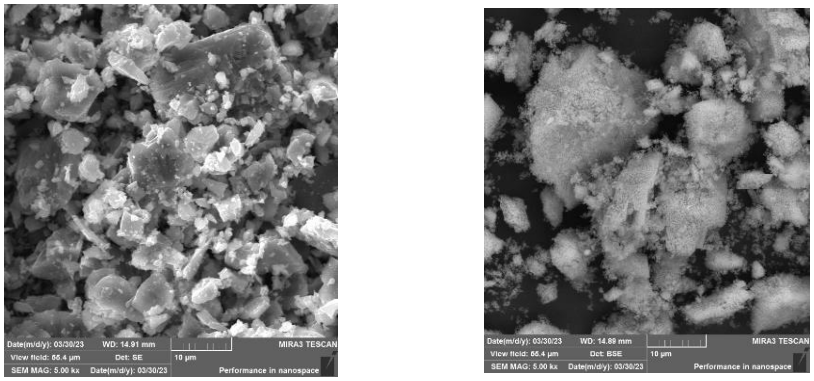

Figure 2 Morphology of the raw dolomite sample ST-1 (left) and sample after repeated DTA/TG analysis after two month of “standing” (right)

The results of DTA/TG analyzes correlate with previous results published by Danková et al. [6]. The recording of the sample TR-1 was almost identical even after two months of the sample "standing". For the sample SED-1, a small peak at a temperature of 400 °C was evident on the DTA curve, corresponding to the hydration of the sample. Higher weight losses were recorded for ST-1 and KRA-1 samples. The endothermic peaks in the temperature range of 350 - 450 °C (corresponding to the $Ca(OH)_2$ phase), present on the DTA records measured immediately after calcination, were more pronounced when measured after two months and slightly shifted to the right to higher temperatures. Individual weight losses correspond to the hydration activity of calcined dolomite and represent only its hygroscopicity, i.e. the ability to bind water molecules from the surrounding environment (air humidity) and do not fully represent its reducing activity [7]. In general, when the hydration activity is higher, the reducing activity is also higher. However, with the same hydration activity, the reduction activity may not be the same, due to the different structure of dolomite.

CONCLUSION

This study confirmed the hypothesis that for the silicothermic reduction of magnesium it is necessary to individually verify the calcination conditions for each sample and determine the influence of hydration activity/active sites in their structure to increase the reduction of Mg.

The DTA/TG analyzes of calcined samples ST-1 and KRA-1 correlated with analyzes of hydrated samples (after two months "standing"), so they appeared as the most suitable samples for the preparation of intermediate products for the production of metallic magnesium.

The results obtained from the laboratory technological processing of dolomites will enable to suggest the methods of magnesium intermediates preparation applicable for semi-operational to operational conditions of metal magnesium production. Given the current crisis situation caused by the lack of critical raw materials, the mentioned laboratory technological research is current and important also from the point of view of the use of high-quality domestic raw material resources, which can be interesting and beneficial especially for manufacturers operating in the Slovak Republic.

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