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Technological research of calcinated dolomite ores as intermediates for metal magnesium production

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Abstract: The current work investigates the differences between four types of calcinated dolomite samples as suitable intermediates for subsequent silicothermic reduction of metal magnesium by simultaneous differential thermal analysis (DTA) /thermogravimetric analysis (TG). The results of the DTA/TG analysis showed the least significant differences at the temperature endotherms with no weight loss on the TG curves at a temperature of 1373 K for the calcined dolomite sample TR-1 from Trebejov deposit. The most significant difference on the DTA curves was detected for the calcinated sample KRA-1 (deposit Kraľovany), which is connected with the hydration activity of the sample. According to the results of the chemical analyses, annealing products of all samples fulfilled two of the three conditions, namely a molecular ratio of CaO:MgO and an impurity content below 2.5% for their subsequent use as feedstocks in the silicothermal process for the preparation of metallic magnesium. Subsequently, the experimental test of silicothermic reduction of magnesium of calcinated sample ST-1 in a flowing argon atmosphere was investigated by EDX analysis. The results indicate that the prepared magnesium sample analysed by EDX – point and mapping analysis confirmed the presence of magnesium totalling 91% despite the failure to reach the temperature in the furnace required for the reduction of Mg.

Keywords: dolomite, annealing, calcined dolomite, DTA/TG analysis

INTRODUCTION

Magnesium is a light metal with high chemical activity of which there are large reserves widely distributed across the globe. Magnesium's excellent properties, principally; light weight, high specific strength; good ductility, damping and machinability; a strong electro-magnetic shielding effect; good shock absorption and good thermal conductivity, means that magnesium is promoted as "the most promising lightweight engineering metal material in the twenty-first century" (Wu et al. 2021).

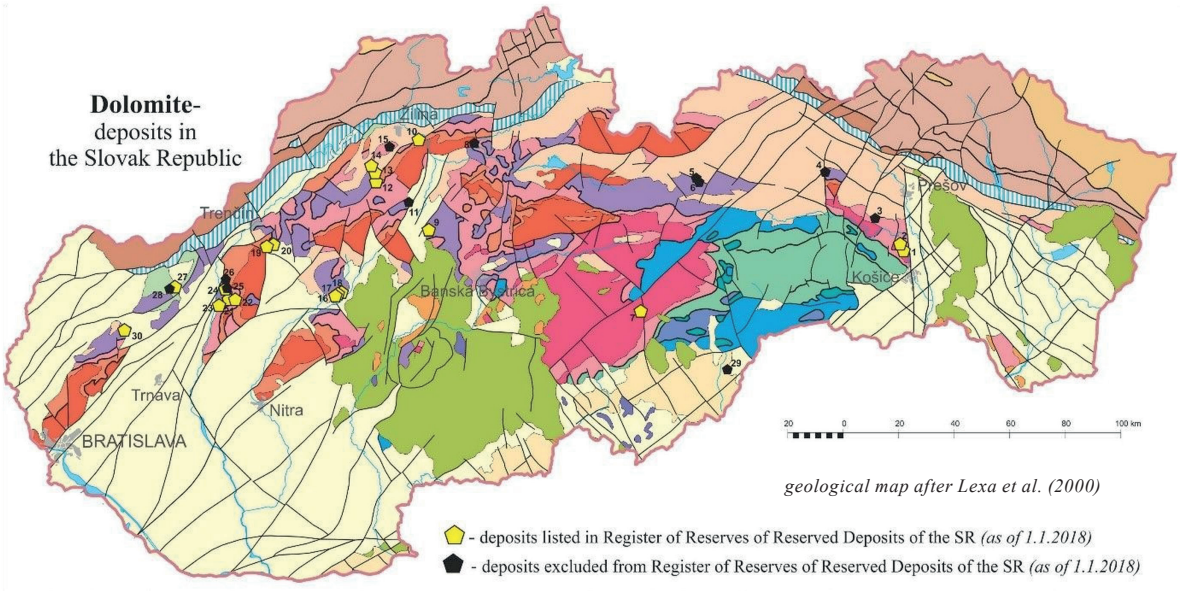
Despite its long history of commercial application, the development of magnesium alloys has been slow compared with those of aluminium alloys. At present, China is the largest producer and exporter of magnesium in the world, accounting for more than 85% of the world's magnesium output. According to the data in recent years, the demand for metal magnesium has been increasing annually, and the domestic supply and demand have reached a balance. Dolomite, and to a lesser extent magnesite, are the key ore minerals in the production of Mg metal by thermal reduction methods. The main advantage of thermal reduction methods is that, under the right conditions, high purity metal (99.95% Mg) is produced. The Pidgeon process is the simplest, oldest, least energy efficient, and most labour-intensive production process.

Most dolomites are secondary sediments that resulted from the metasomatic process between a magnesium-containing solution and limestone.

Only in high salinity lakes can thick dolomites and primary sedimentary dolomites be formed directly. Dolomite is a compound salt mineral composed of magnesium carbonate and calcium carbonate. The theoretical mass fraction is 21.7% dolomite, 30.4% $CaCO_3$, and 47.9% CO_2 (Wu et al. 2021, Zhang et al. 2024).

Dolomites occur in Slovakia in several Middle and Upper Triassic formations or form interbeds, intercalations, or lenses in beds irregularly alternating with surrounding limestones. They occur in many geological formations where tectonic nappes and cover sequences occur. The most important of these are the Middle and Upper Triassic dolomites of the Hron unit, which bear significant dolomite deposits in the Choč nappe of the Strážovská highlands (Fig. 1).

Magnesium is produced by two principal processes: electrolysis of molten magnesium chloride and thermal reduction of magnesia (Sun et al. 2009). The process of extracting magnesium by prefabricated pellets in flowing argon gas was studied by Guo et al. (2020) with the aim of solving the problem of the continuous production of magnesium. The pulverized magnesium and ferrosilicon were mixed with the addition of calcium fluoride and then the mixed powders were compacted into pellets.



Location: 1 - Družstevná pri Hornáde - Malá Vieska, 2 -Trebejov, 3 - Sedlice, 4 - Vyšný Slavkov, 5 - Svit, 6 - Spišská Teplica, 7 - Mútnik, 8 - Kraľovany, 9 - Rakša, 10 - Stráňavy-Strečno-Kosová, 11 -Kláštor pod Znievom, 12 - Rajecká Lesná, 13 - Rajec - Šuja, 14 - Veľká Čierna-Petrová, 15 - Lietavská Svinná, 16 - Malé Kršteňany, 17 -Malé Kršteňany - Chotárna Dolinka, 18 - MK-ChD II, 19 - Rožňové Mitice-Mníchova Lehota, 20 - Trenčianske Mitice, 21 - Modrová, 22 - Modrová - Dolina Rybník, 23 - Hubina, 24 - Lúka, 25 - Lúka II, 26 - Hrádok, 27 - Košariská, 28 - Prašník, 29 - Tornaľa, 30 - Trstín I

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 1.01.2018*

The reduction of calcinated pellets was carried out in a resistant furnace with flowing argon gas. It was found that the reduction reaction would not take place at a temperature below 1273 K. The reduction stage was controlled by means of the diffusion process. The apparent activation energy of silicothermic reduction of the prefabricated pellets was lower than that of the traditional. The diffusion control step of reduction reaction was controlled by the diffusion of Si (Guo et al. 2020).

To date there have been a few experimental research works on magnesium metal production from raw magnesite (Tomášek & Špeťuch 1995, Tomášek et al. 1997).

There were considerations about starting the production of metallic Mg in the Slovak Magnesite Plants in Jelšava in the past but these have not progressed due to economic reasons (Immer 1998).

Previous experiments

Laboratory experiments of the production of metallic magnesium by the silicothermic method was carried out at the SGUDS, in the regional centre of Košice, Slovakia. The technological research of dolomite raw material was focused on the preparation of calcined products in the mixture for the batch for the silicothermic method of obtaining Mg. The CO_2 content in these products was max. 0.3%, the ratio of CaO:MgO components was in the range from 1.1:1 to 1.5:1 and the content of other oxides together with SiO_2 (without CaO and MgO) was below 2.5%. The prepared calcined products of dolomite samples from the deposits Trebejov, Dolný Lopašov, Trstín, Mníchova Lehota, Malé Kršteňany, Hubina and Rajec Šuja meet the above-mentioned required criteria as products for the mixture for the silicothermic method of Mg production. In the calcined products of dolomite lime, the residual CO_2 content was satisfactory, ranging from 0.18 to 0.29%. The ratio of CaO:MgO components was also satisfactory – from 1.37:1 to 1.43:1 and the amount of impurities, contents of SiO_2 and other oxides (except CaO and MgO) was below the required 2.5% limit value (0.81–2.23%). Based on the results obtained of the treatment of dolomites from specific deposits, an estimate of the sources of input raw materials (dolomitic lime) for the silicothermic production of metallic magnesium was made. On the basis of the laboratory-verified suitability of the prepared input raw material from specific deposits together with the experimentally demonstrated ability to obtain metallic magnesium by means of the silicothermic method, an estimate of metallic magnesium sources was made. With the estimated resources of dolomitic lime (164.023 kt) in the studied deposits, according to the average yield (77%), the considered production method (Pidgeon method) is potentially able to recover approx. 31.270 kt of metallic Mg (Bačo et al. 2016).

Preparation of magnesium

Under experimental conditions, it was possible to prepare separate reduced crystals of magnesium. Using equipment of our own design (made on the basis of published structural elements) magnesium was reduced. Its purity was verified on a microanalyzer and ranges of up to 96% Mg, were achieved (Fig. 2). The suitability of the prepared intermediate product from a specific bearing was thereby verified in practice. The theoretically usable amounts of metallic magnesium obtained from the dolomites of the deposits point to the possible multiple values of this raw material (Kollová et al. 2023).

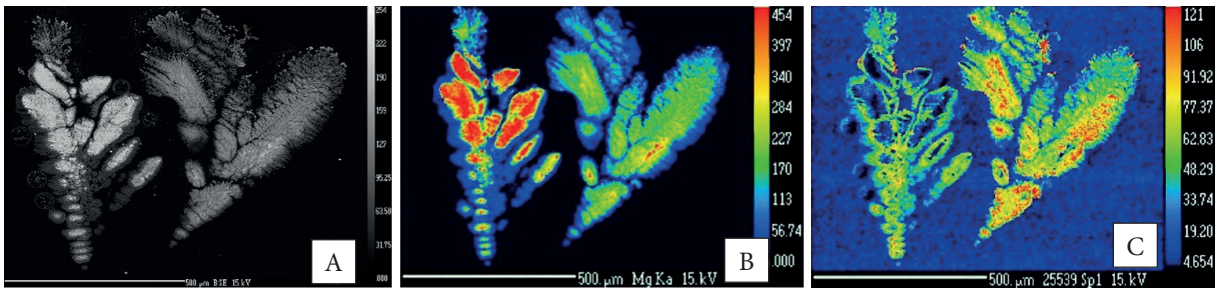


Fig. 2. *Appearance of individual magnesium metal crystals and their intergrowths clearly visible on BSE (A); distribution maps of Mg (B) and O (C). BSE images and distribution maps – P. Konečný*

The reduction activity of magnesium in the silicothermic process depends on the quality of prepared calcined products, where the hygroscopicity of calcined dolomite plays a very important role (Che et al. 2020).

In this paper, the calcination products from four samples of dolomite originating from different Slovak deposits are analysed by means of the DTA/TG method. The aim of the study is to define a suitable thermal treatment of dolomite ore for further silicothermic reduction in flowing argon to prepare magnesium metal according to the Pidgeon process, but without a vacuum. An advantage of the Mg reduction from dolomite ore is also the proximity of the dolomite deposit (Stráňavy) at the manufacturer of ferroalloys in Orava region (Slovakia).

The results obtained can help with clarifying how calcination temperatures and time can influence the reduction of metallic magnesium and form various type of dolomites.

EXPERIMENTS

Raw materials

For experimental purposes, dolomite ores from the Slovak deposits: Sedlice (SED-1), Trebejov (TR-1), Stráňavy (ST-1) and Kraľovany (KRA-1) 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 below 8.0 mm. All samples were subsequently homogenized and quartered. From each raw sample individual homogeneous parts were prepared for further laboratory processing.

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° 2θ, step 0.01°, time 0.3 s/step. Processing and evaluation of measured data were realized using DIFFRAC.EVA V3.1. software. Measurement is 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 analyses (DTA/TG analysis). Measurements were made under the following conditions: heating range: 297–1273 K, heating rate 283 $K \cdot min^{-1}$, reference material: powdered Al_2O_3, crucibles: ceramic Al_2O_3, furnace atmosphere: N_2 circulation: 20 $mL \cdot min^{-1}$.

Input samples of raw materials and processed intermediates/products were subjected to chemical analysis in the geoanalytical laboratories of the SGUDS in Spišská Nová Ves.

Experimental procedures

Annealing tests of dolomite samples were carried out in an electric laboratory furnace ELOP-1200/15. The crucibles were placed in a muffle furnace and then the furnace was heated up continuously from room temperature to 1273 K and 1373 K (the heating rate was 283 $K \cdot min^{-1}$) with a holding time for 1 h and 2 h. The products of calcination obtained at different temperatures were taken out and stored in a desiccator before DTA/TG analyses were carried out.

Experimental test of magnesium reduction

A dolomite sample ST-1 from the Stráňavy locality was selected for the experimental test. The dolomite sample was calcined at a temperature of 1423 K for 1.5 h in powder form. It was then mixed with powdered FeSi and CaF_2 in a ratio of 77.5:17.5:5 and pressed into a tablet with a diameter of 13 mm and thickness of 5 mm. The experiment was carried out in an electrically heated horizontal tube furnace with flowing argon. The tablet was placed in the furnace for 2 h at 1073 K for degassing and reduction was carried out for 4 h at a higher temperature of 1373 K.

RESULTS AND DISCUSSION

DTA/TG and chemical analyses

Raw samples of dolomite used for laboratory experiments were of high purity. The CaO content varied from 30.3 to 30.7% and MgO content was in the range from 20.9 to 21.4% for the studied samples, see Table 1. Higher SiO_2 content was analysed

for raw samples SED-1 and TR-1. The highest contents of other oxides (impurities) were determined for sample TR-1. Despite small differences in the content of impurities, the XRD diffractograms are very similar for all of the studied samples, where the presence of the main mineral phase of dolomite was confirmed (Fig. 3).

In order to obtain suitable annealed products of dolomitic lime CaO·MgO, raw samples with a grain size below 8.0 mm were annealed at temperatures of 1273 K and 1373 K for 1 h and 2 h. DTA/TG analyses were performed immediately after cooling the samples, due to the rapid hydration of the samples. In general, calcined dolomites are highly hydrophilic which can reduce their activity and then reduce the yield of magnesium. The formation of the portlandite phase is more obvious than the brucite. Besides, exposing $Ca(OH)_2$ and $Mg(OH)_2$ in the air for a long time, the former absorbing CO_2 further from air to become $CaCO_3$ is more easily than latter to generate $MgCO_3$ (Che et al. 2020).

The products after annealing were subjected to chemical analysis and were evaluated with regard to the required conditions for calcined dolomite, so that the molecular ratio of CaO:MgO is in the range of 1.1:1 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). The activity of calcined dolomite refers to the amount of active MgO in calcined dolomite. When the ignition loss of calcined dolomite is greater than 0.5%, it has a serious effect on the vacuum in the tank. At the same time, this also causes the formed H_2O and CO_2 to react with magnesium vapor and decreases the reduction rate.

Table 1

Chemical composition of dolomite raw samples [wt.%]

Sample	CaO	MgO	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	Na_2O	K_2O	P_2O_5	CO_2	a.l. [%]
SED-1	30.3	20.9	1.07	<0.01	0.16	0.20	0.01	<0.2	<0.05	<0.01	46.7	47.3
TR-1	30.4	21.0	1.02	0.02	0.42	0.24	<0.01	<0.2	0.05	0.01	46.8	46.8
ST-1	30.7	21.2	0.32	<0.01	0.12	0.08	0.01	<0.2	<0.05	0.01	41.4	47.5
KRA-1	30.6	21.4	0.12	<0.01	<0.05	<0.05	<0.01	<0.2	<0.05	<0.01	46.6	47.7

a.l. – annealing loss.

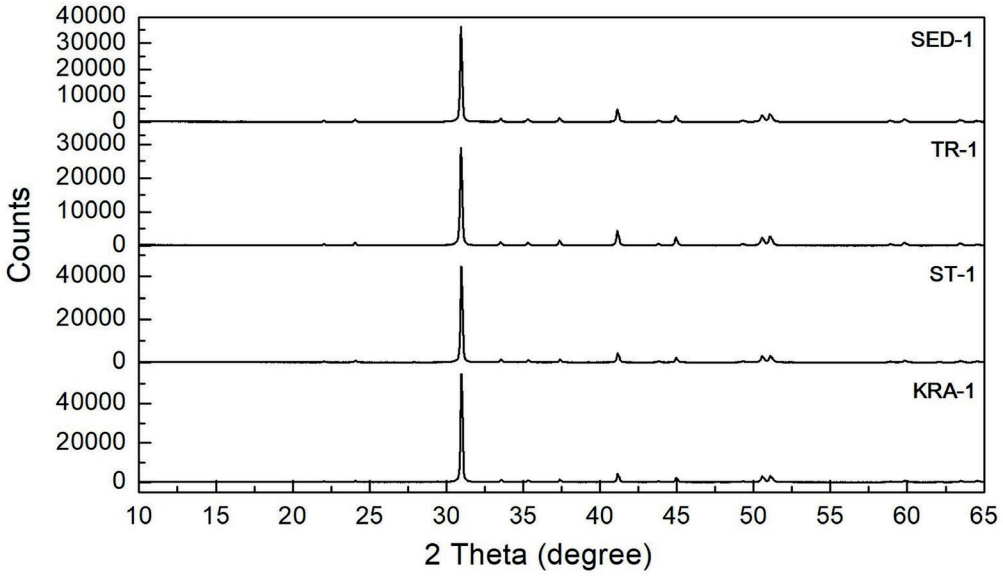


Fig. 3. *XRD analysis of dolomite raw samples*

In addition, when the contents of other impurities such as SiO_2 and Al_2O_3 are too high, they form slag with CaO and MgO, and this correspondingly reduces the activity of MgO. Meanwhile, impurities cause nodules in slag and then cause difficulties in operation. When the total amount of K_2O and Na_2O in the pellets is greater than 0.15%, oxidation-combustion loss occurs if there is metal magnesium in the reduction tank. This thereby reduces the actual yield of magnesium.

For all of the annealed samples, a satisfactory ratio of CaO:MgO components was achieved, as well as the amount of impurities (Table 2). The residual CO_2 content varied from 0.29 to 0.59%.

The SiO_2 content decreased after annealing for all studied samples, the highest amount was analysed for sample TR-1. The content of other impurities was also the highest for this sample after heat treatment (see Table 2).

Differences in the DTA curves for calcined dolomites related to SiO_2 or CaO content in thermally modified samples (Table 2), and their microstructure.

For all samples, the peaks observed on the DTA curves in the temperature range 663–723 K correspond to the preferred formation of portlandite phase against brucite (Figs. 4A–7A). From the TG curves, no weight loss was observed for the samples annealed at 1373 K, indicating the required decomposition of $CaCO_3$. The slight weight loss detected on the TG curves of the samples annealed at 1273 K corresponded to the loss of CO_2 (Figs. 4B–7B).

Table 2
Chemical composition of calcinated dolomite samples at 1373 K [wt.%]

Sample	CaO	MgO	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	Na_2O	K_2O	P_2O_5	CaO:MgO	ΣR_2O_3
Sample annealed at 1373 K/1 h												
SED-1	30.6	21.7	0.21	<0.01	0.14	0.07	<0.01	<0.2	<0.05	<0.01	1.41	0.86
TR-1	30.1	21.3	0.88	0.02	0.41	0.23	<0.01	<0.2	<0.05	0.01	1.41	2.06
ST-1	30.8	21.6	<0.05	<0.01	<0.05	0.08	<0.01	<0.2	<0.05	<0.01	1.43	0.37
KRA-1	30.8	21.7	<0.05	<0.01	<0.05	<0.05	<0.01	<0.2	<0.05	<0.01	1.42	0.40
Sample annealed at 1373 K/2 h												
SED-1	30.5	21.5	0.26	<0.01	0.16	0.09	<0.01	<0.2	<0.05	<0.01	1.42	0.99
TR-1	30.2	21.3	0.91	0.02	0.39	0.22	0.01	<0.2	<0.05	0.01	1.42	2.04
ST-1	30.7	21.6	0.07	<0.01	<0.05	<0.05	<0.01	<0.2	<0.05	<0.01	1.42	0.58
KRA-1	30.7	21.7	<0.05	<0.01	<0.05	<0.05	<0.01	<0.2	<0.05	<0.01	1.41	0.59

ΣR_2O_3 – sum of SiO_2 and other oxides without CaO and MgO max. 2.5%; CO_2 max. 0.30%; CaO:MgO from 1.1:1 to 1.5:1.

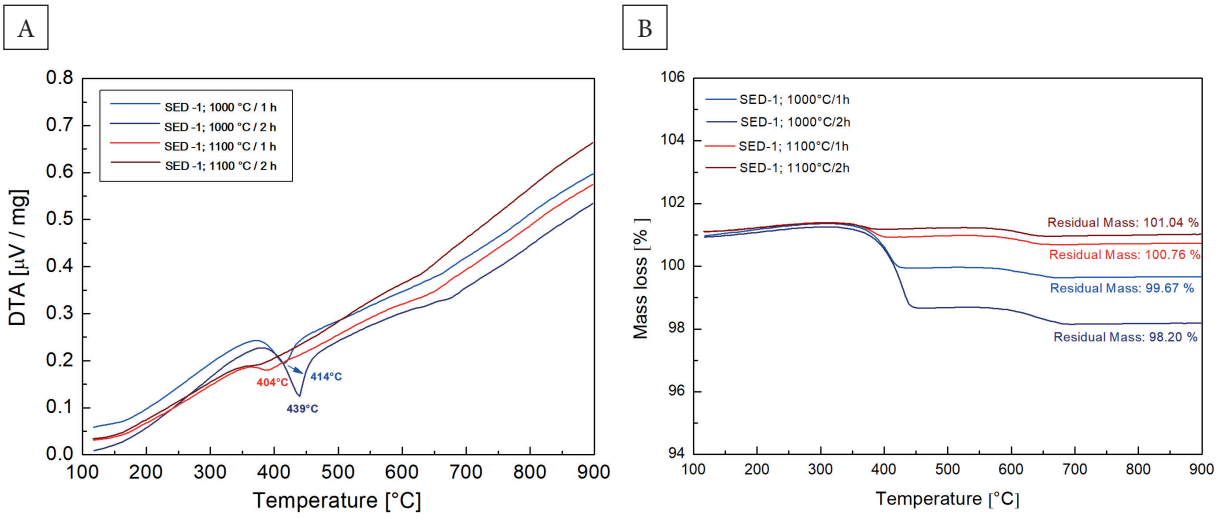


Fig. 4. *DTA curves of calcined dolomite sample SED-1 (A); TG curves of calcined dolomite sample SED-1 (B)*

The SED-1 sample after annealing at 1373 K for 2 h was characterized by an almost smooth DTA curve, which indicates a suitable content of CaO, MgO and impurities in the analysed product. It is likely that the hydration of the sample did not occur as rapidly as for the samples annealed for shorter periods and/or at lower temperature (Fig. 4A).

The highest SiO_2 content in the annealed sample TR-1 affected the shape of its DTA curves. As the content of oxide impurities increases, the temperature required for decomposition decreases, which was confirmed by obtained endotherms (Fig. 5A). For the samples annealed at 1273 K, no significant differences in endotherms were detected on the obtained DTA curves considering the calcination time (Fig. 5). From the TG curves, the smallest differences in weight loss were detected depending on the temperature and time of calcination compared to the other samples (Fig. 5B).

For the sample ST-1, more significant differences as a function of calcination temperature were observed from the obtained DTA curves. The clearest endothermic peak was observed on the DTA curve at a temperature of 723 K of the sample annealed at 1273 K for 2 h, which corresponded with the presence of the portlandite phase. Regardless of the calcination time, the DTA curves for the sample annealed at a higher temperature were almost identical (Fig. 6A).

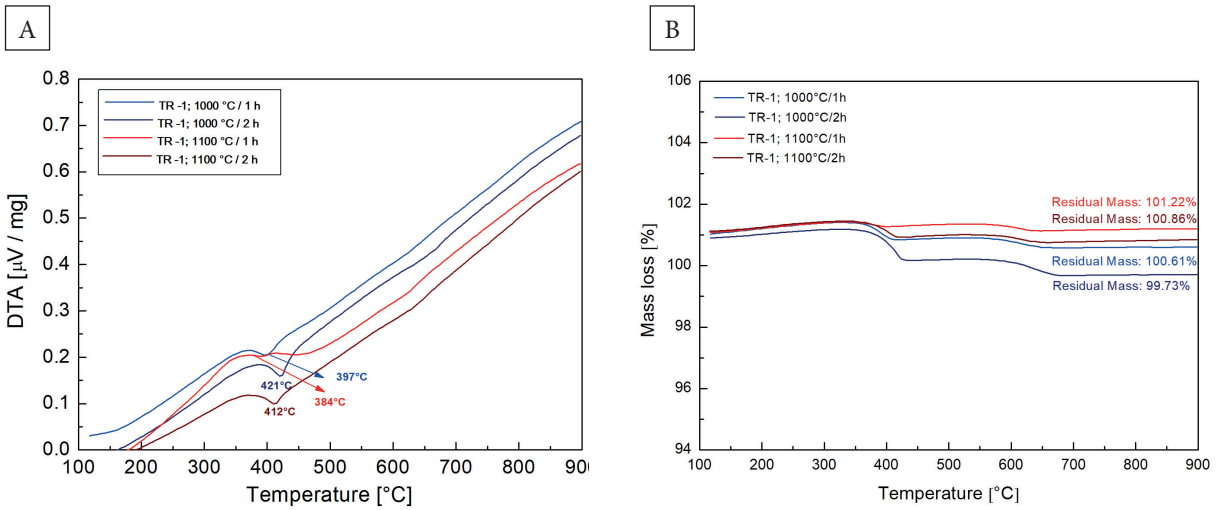


Fig. 5. *DTA curves of calcined dolomite sample TR-1 (A); TG curves of calcined dolomite sample TR-1 (B)*

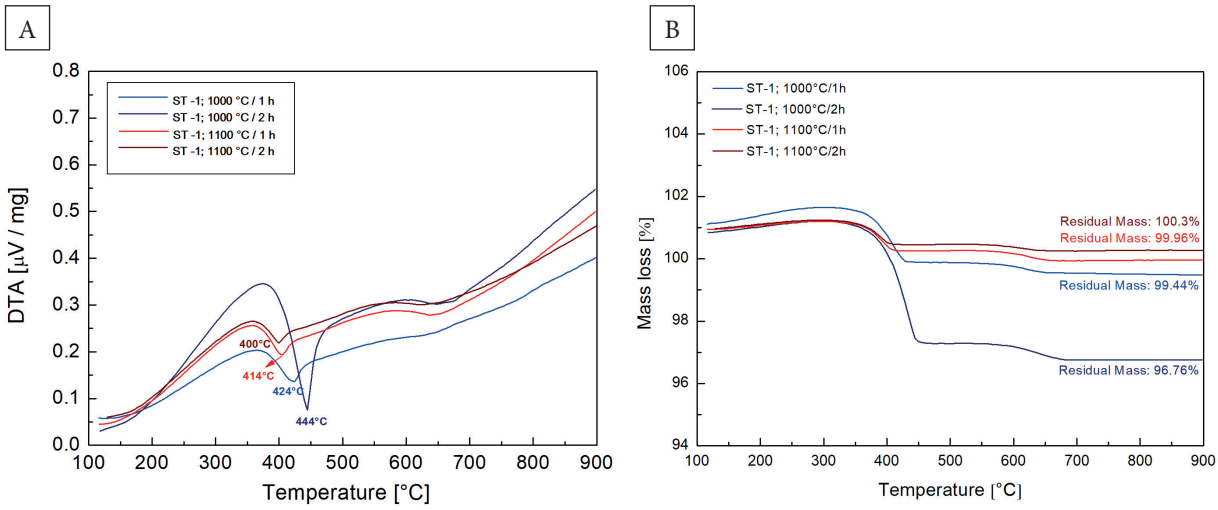


Fig. 6. *DTA curves of calcined dolomite sample ST-1 (A); TG curves of calcined dolomite sample ST-1 (B)*

The endothermic peaks were shifted to the left, to a lower temperature of about 673 K. In the temperature range of 1146–1246 K, an indication of the second endothermic peak was also observed, associated with the decomposition of $CaCO_3$ by the reverse reaction of $Ca(OH)_2$ with CO_2 (from air). The TG curves of the sample correlated with the DTA analyses, where the greatest mass loss was observed for the sample annealed at 1273 K for 2 h (Fig. 6B).

The most significant differences in the DTA analyses were obtained from the annealed sample KRA-1 (Fig. 7A). Similar to the ST-1 sample, sharp endothermic peaks for annealing at 1273 K were observed on the DTA curves, which is probably related to the higher CaO content in the samples (Figs. 6A, 7A). Calcination at higher temperature resulted in a smaller, broader peak shifted to the left on the DTA curve, to around 673 K. The endothermic peaks are related to the hygroscopicity of the sample.

From the previous study, the dolomite samples were annealed at 1323 K for 2.5 h and kept in the laboratory for a longer time without a protective atmosphere or vacuum. The TG analyses confirmed higher amounts of their weight loss: 29.32% (SED-1); 27.86% (TR-1); 33.73% (ST-1); 33.72% (KRA-1), which corresponds to their hydration activity (Bekényiová et al. 2024). When the activity of calcined dolomite is between 30 and 35%, the magnesium output increases significantly. This weight loss corresponds to the hydration activity of calcined dolomite and only represents its hygroscopicity and does not fully represent its activity in reduction. During calcination, CO_2 is removed from the raw dolomite, the calcined dolomite is porous, has a higher surface area, high reactivity, and is hygroscopic. Hygroscopicity as a material's ability to absorb moisture from the environment is important because of magnesium yield. The difference between the hydration activities of various kinds of calcined dolomite should be slight, but their activities in reduction should also be very different. Generally, when hydration activity is higher, the reduction is higher. However, for the same hydration activity, the activity in reduction is not necessarily the same because of the different dolomite structures (Zhang et al. 2024). Therefore, the annealing conditions need to be verified for each sample individually for their next application for silicothermic reduction of magnesium.

The endothermic peaks were sharper for samples ST-1 and KRA-1 annealed at both temperatures. Also, the decomposition of $CaCO_3$ by the back reaction of $Ca(OH)_2$ with CO_2 was detected in the temperature range around 873–973 K. However, no weight loss was observed from the TG curves for samples annealed at lower temperature, indicating the required decomposition of carbonates in the obtained products.

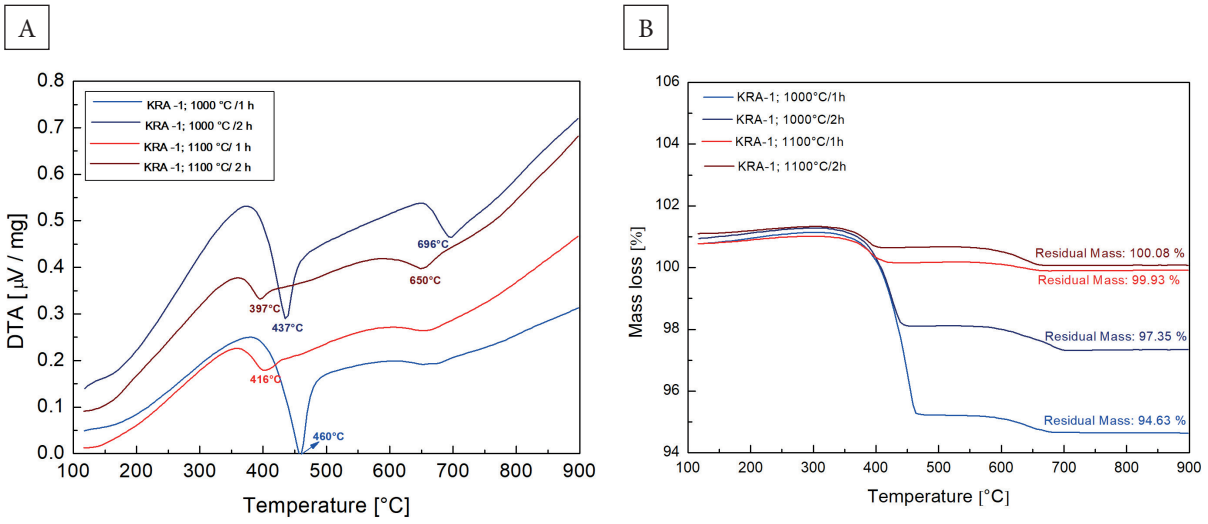


Fig. 7. *DTA curves of calcined dolomite sample KRA-1 (A); TG curves of calcined dolomite sample KRA-1 (B)*

The higher CO_2 content in calcined samples determined from chemical analyses was not confirmed by TG analyses. Different studies in the field of metallic magnesium preparation show that not as much emphasis is currently placed on the requirement of maximum permissible content of CO_2 in the calcined intermediates for the preparation of magnesium metal. The Pidgeon process requires calcined dolomite that has higher activity because a better quality of calcined dolomite is beneficial for the reduction reaction. Therefore, for future industrial processing, it will be advisable to investigate and validate optimum calcination temperatures. Thermal treatment also ensures higher stability of the obtained intermediates for their further applications in the production of magnesium metal.

SEM analysis

The formation of the desired intermediate was also indirectly confirmed by observing the morphology of the annealed samples by scanning electron microscopy. The input sample of dolomites was compared to samples after annealing at a temperature of 1373 K with a holding time of 2 h and immediate DTA analyses. In the input sample ST-1 a larger number of calcite particles with smooth layered surfaces was observed (Fig. 8A). In the sample annealed at 1373 K, there were marked change in the surface, with significantly smaller and agglomerated particles of dolomitic lime observed (Fig. 8B).

Experimental test of magnesium reduction

Based on the results of DTA/TG analyses, an experimental test was performed where we verified several factors that can influence magnesium reduction. The temperature achieved in the new laboratory furnace did not reach the required temperature for magnesium reduction. The boiling point of magnesium is 1363 K and an even higher temperature is required for reduction because the principle of thermal reduction of Mg (using FeSi) metallic magnesium, formed in the process, evaporates and then condensates away from the hot region. The available laboratory equipment only allowed for a temperature of about 1373 K. Although the preferable temperature required for reduction is about 1473–1573 K, the laboratory test did help to verify the suitability of the input material for the production of magnesium metal. The prepared magnesium sample was analysed by EDX – point and mapping analysis, which confirmed the presence of magnesium metal at a level of 91% (Figs. 9A, B, 10).

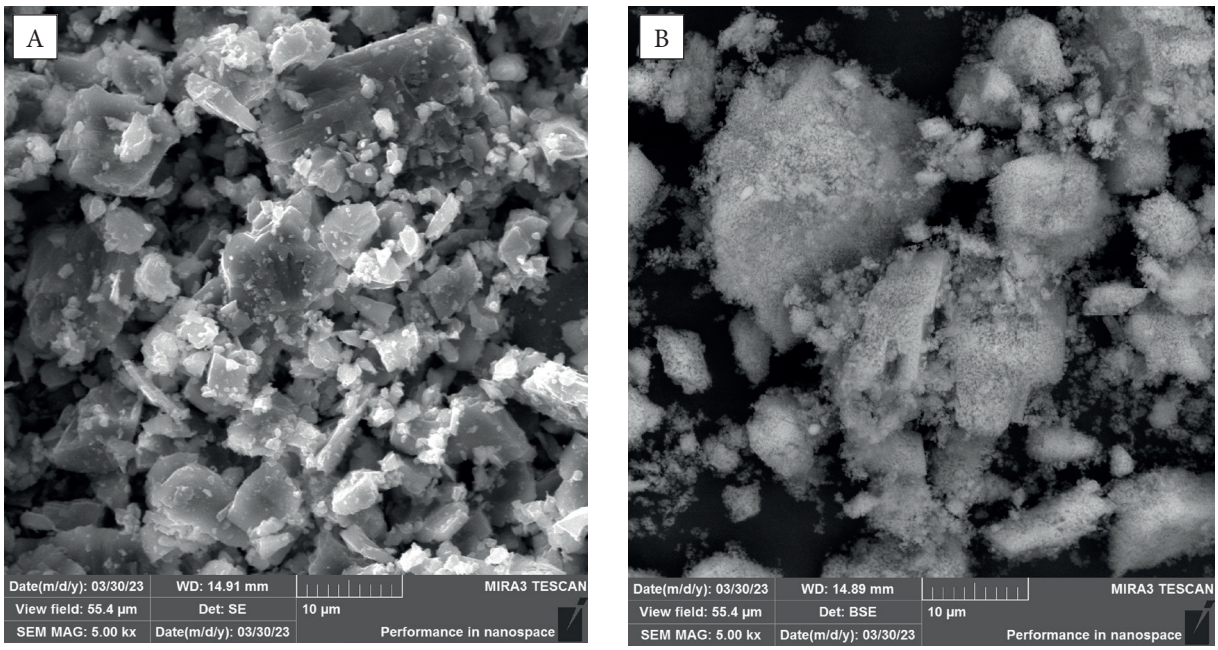


Fig. 8. *Morphology of the input sample ST-1 observed by SEM (A); morphology of calcined dolomite particles, sample ST-1 annealed at 1373 K/2 h (B)*

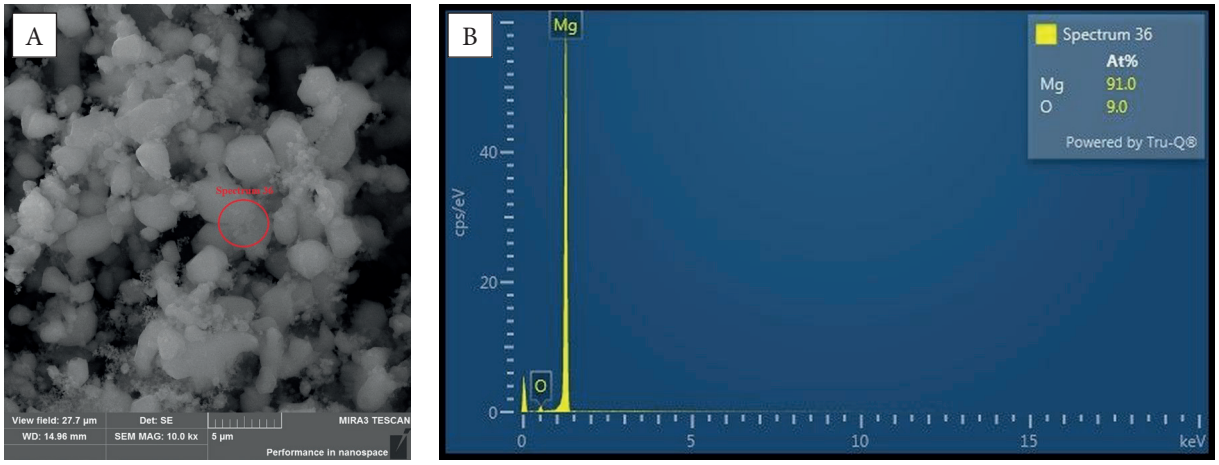


Fig. 9. *Morphology of prepared magnesium metal sample with marked part of the EDX analysis (A); EDX analysis of the prepared magnesium (B)*

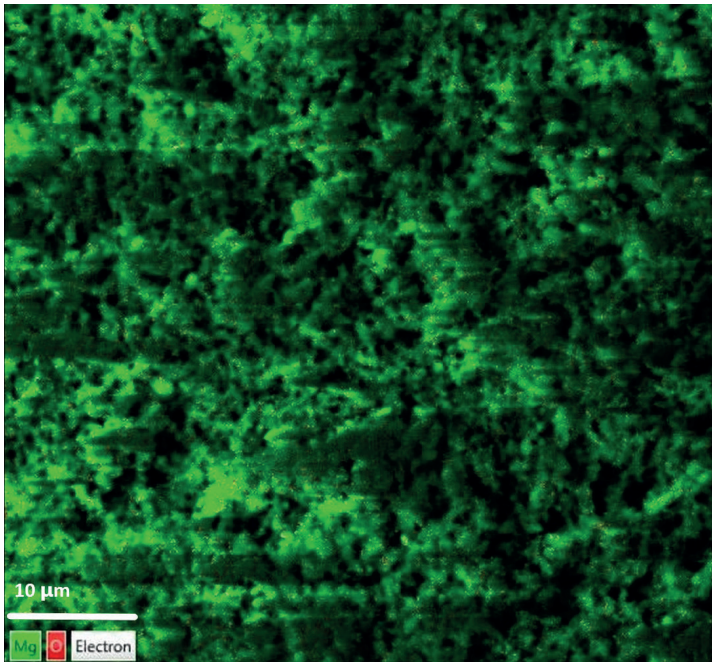


Fig. 10. *Morphology of prepared magnesium metal sample in mapping mode*

CONCLUSIONS

Samples of raw dolomite ore from four Slovak deposits were calcined at 1273 K and 1373 K for 1 h and 2 h and analysed by the DTA/TG method to specify the conditions and better characterize the dolomite lime preparation process. For the samples annealed at higher temperatures, endothermic peaks of around 673 K, corresponding to the portlandite phase, were observed on the DTA curves. For the samples annealed at 1273 K, these peaks were more expressive, shifted to the higher temperatures on the DTA curves and related to the faster hydration of samples. Based on the obtained results, it can be assumed that the samples calcined at a higher temperature are more stable. However, the hydration activity of calcined dolomite only represents its hygroscopicity and does not fully represent its reduction activity.

The results of DTA/TG analysis pointed to the most suitable samples for the preparation of intermediate products – samples ST-1 and KRA-1. 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 Mg.

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