

RESEARCH PAPER

SILICOTHERMIC REDUCTION OF THANH HOA DOLOMITE: THERMODYNAMIC AND EXPERIMENTAL

Quyen V. Vu¹⁾, Trang T. T. Vu²⁾, Cuong M. Doan³⁾, Binh N. Duong^{1)*}, Huy D. Tran^{1)*}

¹⁾ School of Materials Science and Engineering, Hanoi University of Science and Technology, Hanoi, Vietnam

²⁾ Vietnam Maritime University, Haiphong, Vietnam

³⁾ University of Information and Communication Technology, Thai Nguyen, Vietnam

* Corresponding author: binh.duongnec@hust.edu.vn, tel.: +84 973 002988, huy.tranduc@hust.edu.vn, tel.: +84 945 697679, School of Materials Science and Engineering/Hanoi University of Science and Technology, Hanoi, Vietnam

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ABSTRACT

Thermodynamic and experimental studies were carried out on the process of Calcinated Thanh Hoa dolomite reduction to produce magnesium. Thermodynamically studied the effect of pressure and temperature on reduction was carried out together with a verification experiment. Results show that at the appropriate temperature and vacuum pressure, Calcinated Thanh Hoa dolomite can be reduced using ferrosilicon as the reductant. The higher level of vacuum, the lower temperature required for reduction. Thermodynamic calculation pointed out that at a vacuum pressure of 600 Pa, the reduction temperature could be as low as 1140 °C. Experiment results indicated that although reduction could be done at 1150 °C, the process efficiency was low, generally below 20%. Process efficiency enhanced as temperature increase and reaches the highest value of 85,8% at 1250 °C (25 wt.% ferrosilicons). The amount of ferrosilicon used also has influenced the process efficiency. After three hours of reduction, the obtained magnesium was very high in purity, 99.3%.

Keywords: Thanh Hoa Dolomite, Silicothermic Reduction, Pidgeon Process, Thermodynamic, Magnesium Production

INTRODUCTION

Magnesium is a light metal that has huge potential to be used as structural materials. Magnesium and its alloys have been found in many structural applications such as in electric and electronic devices, biomedical, home appliance and automobile vehicle [1-8]. Magnesium could be produced from various type of ores such as magnesite, dolomite, bischofite, carnallite, and serpentine. The metal could also be electrowon from brine or seawater [9, 10]. One of the most popular sources uses in the current magnesium production industry is dolomite [11, 12]. It is an anhydrous carbonate mineral composed of calcium magnesium carbonate which has the ideally chemical formula of $\text{CaCO}_3 \cdot \text{MgCO}_3$ or $\text{CaMg}(\text{CO}_3)_2$.

The major part of magnesium metal production is conducted via the Pidgeon process which is a metallothermic reduction process [13]. In this process, magnesium was reduced from calcined dolomite under a vacuum atmosphere using silicon as a reductant and calcium fluorite as the catalyst. There are several noticeable benefits of the Pidgeon process that includes simple operation, high magnesium purity and low capital investment [10]. In the Pidgeon process, silicon was used as the reductant for the reduction of calcined dolomite ($\text{CaO} \cdot \text{MgO}$). Calcined dolomite was preferred as the raw material because of the presence of CaO, it reacts with SiO_2 and forms $\text{CaO} \cdot \text{SiO}_2$ during reduction. The presence of $\text{CaO} \cdot \text{SiO}_2$ has limited the formation of $\text{MgO} \cdot \text{SiO}_2$ not only improves the reduction efficiency but also easier the reduction of Mg from MgO [14]. A raw material that contains only MgO, therefore, cannot be

used in this process because of the formation of $\text{MgO} \cdot \text{SiO}_2$ stop the reducing reaction.

In Vietnam, the development of supporting industry for electric & electronic, home appliance and automobile manufacturer has led to a rapid increasing in magnesium and magnesium alloys demand. However, Vietnam industries have yet to be able to produce the metal and its alloys, all the magnesium metal and its alloys in uses were imported. Dolomite is widely available in Vietnam but most of the mined dolomite was used as construction materials, refractory materials and as an additive in the iron & steel making process. Calcinated Thanh Hoa dolomite which contains approx. 39 % MgO and 59 % CaO are considered to suit the production of magnesium.

In this work, thermodynamically studied the effect of pressure and temperature on calcined Thanh Hoa dolomite reduction was carried out. Reduction experiments were performed for verification of the thermodynamic calculation and also to study the feasibility of Mg production from calcinated Thanh Hoa dolomite. The effect of other factors on reduction such as the amount of reductant used and the CaO addition was also investigated.

MATERIAL AND METHODS

Dolomite ore used in this study was obtained from a dolomite mine at Rong mountain, Thanh Hoa province, Vietnam. Other raw materials such as ferrosilicon and calcium fluorite were commercially available. The reaction module of FactSage software is used to calculate the pressure-temperature (P-T) relationship for the reducing reactions. Thermodynamic

databases were from the software itself, including FactPs, FToxid, FTsalt databases [15]. Ferrosilicon used for reduction was ground to approx. 100 µm in particle size. The chemical composition of the ferrosilicon is shown in **Table 1**. XRD analysis indicated that the ferrosilicon mainly consists of Si and FeSi₂ phase (**Fig. 1**).

Table 1 Composition of ferrosilicon

Component	Si	C	P	S	Fe
Wt. (%)	72.0	0.1	0.03	0.02	balance

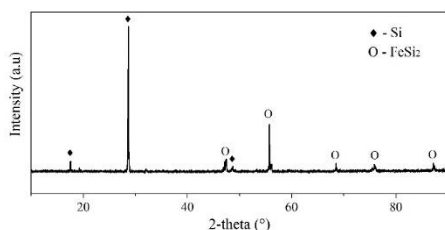


Fig. 1 XRD pattern of ferrosilicon used for reduction

The experimental procedure is shown in **Fig. 2**. Firstly, dolomite ore was crushed into particles of 3 to 4 cm in size and then calcined at 1100 °C for 4 hours. The calcined dolomite then ground to approx. 100 µm in particle size using a ball mill. The composition of the calcined dolomite is shown in **Table 2**.

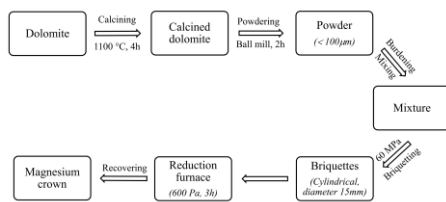


Fig. 2 Process of preparing magnesium from Thanh Hoa dolomite

Table 2 Composition of calcined dolomite

Component	SiO ₂	Fe ₂ O ₃	MgO	CaO
Wt. (%)	0.30	0.15	38.89	58.73

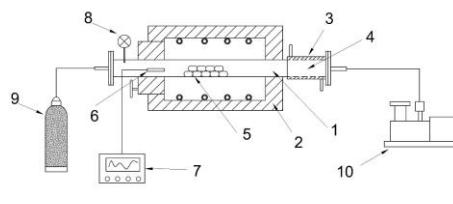


Fig. 3 Reduction apparatus. 1-Stainless steel retort; 2- Furnace with electric heating element; 3-Water jacket; 4-Mg condensation section; 5-Briquettes of raw materials; 6- Thermocouple; 7- Temperature control system; 8- Vacuum gauge; 9-Inert gas supply; 10-Vacuum pump

The obtained calcined dolomite was mixed with ferrosilicon (FeSi) reductant and 3 wt.% CaF₂ catalysts [16, 17]. The

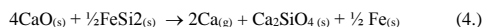
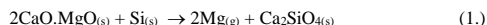
mixture then mounded into a cylindrical mould of 15 mm in diameter and pressed at 60 MPa using a hydraulic press [18]. After that, the pellets were removed from the mould and placed in a stainless-steel horizontal vacuum reduction tube for reduction. A diagram of the reduction furnace is shown in **Fig. 3**.

The reduction was carried out for 3 hours at a certain temperature and the vacuum pressure was kept at a constant of 600 Pa. At the end of the reduction process, Ar gas is introduced into the retort to balance the pressure and to protect the Mg product. After that, the remained pellets and Mg products were taken out for characterization. The process efficiency was calculated based on the mass of Mg product and Mg in raw materials before reduction.

RESULTS AND DISCUSSION

Thermodynamic study of calcinated Thanh Hoa's dolomite reduction

Possible reducing reaction of calcinated dolomite are following:



According to Dalton's law for partial pressure, it can be considered that $P_{\text{Mg}} \approx P$ because of the vapour state of magnesium (P is the vacuum pressure in general) and assumed that the activity of all reactants are approximately equal to one (1) due to their pureness and thus, Gibbs free energy of the system is a function of pressure and temperature. Using thermodynamic data of the compounds and calculation, it's possible to determine the pressure and temperature at which the Gibbs free energy of a reaction is equal to zero. A pressure-temperature (P-T) curve built at the Gibbs free energy of a reaction (ΔG) equal to zero divides the P-T diagram into two parts, the area above the curve indicates that at these values of pressure and temperature, ΔG of the reaction is sub-zero. Therefore, the area under the curve indicates that at these values of pressure and temperature, ΔG of the reaction is positive. **Fig. 4** shows the pressure-temperature (P-T) curve built for reaction (1), (2), (3), and (4).

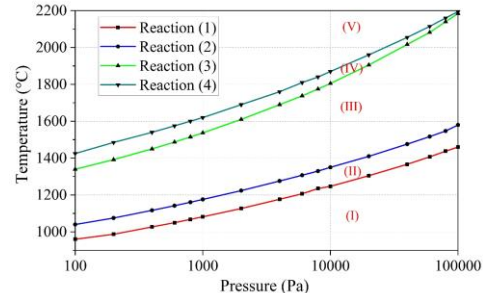


Fig. 4 P-T curves of reaction (1- 4)

As depicted in **Fig. 4**, when the pressure and temperature values fall in the (I) area, none of the reaction occurs. Nevertheless, when the pressure and temperature values fall in the (V) area, all of the above reactions tend to occur. In general

reduction, reaction (1) and (2) are favourable while reaction (3) and (4) should be limited. Thus, the values of pressure and temperature for the reduction of dolomite should be picked in the III area.

At the value of pressure pre-picked at 600 Pa, the reducing temperature should be in the range of 1140 to 1480 °C. Analysis of the changes in main products during the reducing process was carried out and the results are shown in Fig. 5. When using only 17% ferrosilicon, the formation of magnesium was not completed until approx. 1250 °C, as there was still a small increase appears on the Mg line when temperature increases from 1200 to 1250 °C. Increase the amount of ferrosilicon used for reduction to 20, 25, and 30% and this small step disappear, all possible Mg was formed at approx. 1100 °C. A higher amount of ferrosilicon also resulted in the formation of Fe_3Si_7 , the more ferrosilicon used, the more Fe_3Si_7 formed.

As presented in Fig. 5, Ca and SiO vapours were formed at high temperature (1300 °C), the amount of both Ca and SiO vapours increased as temperature increases. These vapours might contaminate the magnesium product [19]. In another study, CaF_2 was reported to start evaporating at approx. 1260 °C and limiting the efficiency of the reductant [20].

Calcinated Thanh Hoa's dolomite reduction experiment

Based on the above theoretical analysis, the pressure for experimenting with the reduction of calcinated Thanh Hoa dolomite was pre-picked at 600 Pa and the temperature was varied from 1050 -1300 °C. The amount of ferrosilicon used were 13, 17, 20, 25, and 30%.

Effect of the reducing temperature and ferrosilicon content.

The effect of temperature on the reduction efficiency is shown in Fig. 6. The reducing reactions were all endothermic and

thus, the higher temperature, the faster reduction. In addition, from the thermodynamic point of view, the reduction temperature needs to reach a minimum value for the free energy of the reaction to become sub-zero ($\Delta G < 0$). According to thermodynamic calculation, at a vacuum pressure of 600 Pa, the minimum reduction temperature for the spontaneous reaction is 1045 °C. However, as depicted in Fig. 6, the reaction efficiency is relatively low. As the temperature increases, the reduction efficiency rapidly increased. The obtained results show that the magnesium reduction efficiency is divided into two stages. As can be seen with samples containing 25% ferrosilicon, in the first stage the efficiency increases rapidly from approx. 20 to 65% when temperature raised from 1050 to 1100 °C and reached 81% at 1200 °C. In the second stage, the reduction efficiency slowly increases and reaches the maximum value of approx. 86% at 1250 °C. Raising the temperature to 1300 °C did not improve reduction efficiency.

As discussed in the thermodynamic analysis, at 1050 °C and vacuum pressure of 600 Pa, only reaction (1) occurs and thus, resulted in low reduction efficiency. The increasing temperature then facilitated reaction (2), resulting in a significant improvement in reduction efficiency. However, the high temperature might also facilitate unwanted reaction (3) and (4). Theoretically, the required amount of ferrosilicon needed for the reaction was approx. 17%. As depicted in figure 6, higher reduction efficiencies were obtained with raw materials which have more than 17% of ferrosilicon. The highest reduction efficiency was approx. 86% at the ferrosilicon content of 25%. At higher ferrosilicon content, reduction efficiency somehow reduced. Too much Si available might result in the formation of Si-Mg compound like the $\text{MgO} \cdot \text{SiO}_2$ as discussed above. The compound has traped Mg and hampered reduction efficiency.

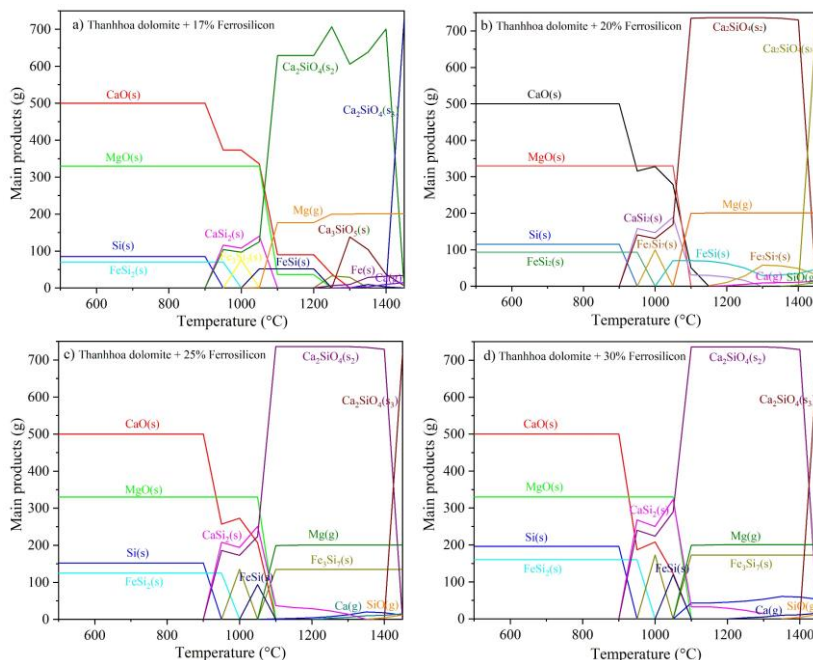


Fig. 5 Thermodynamic analysis of reduction with a) 17% ferrosilicon, b) 20% ferrosilicon, c) 25% ferrosilicon, and d) 30% ferrosilicon

Fig. 7 shows the XRD patterns of the remaining briquettes after reduction (the residue) at 1200 °C for 3 hours. As can be seen, with 17% of ferrosilicon, the residue contains only Ca_2SiO_4 as the reaction product, CaO , MgO , and Fe_2O_3 were unreacted leftover from the raw material. At 25% of ferrosilicon, $3\text{CaO} \cdot 2\text{SiO}_2$ was found in the residue beside Ca_2SiO_4 . This complex oxide formation could be the consequence of the increasing ferrosilicon in the mixture. The extra silicon was oxidized to silica and the silica tends to react with Ca_2SiO_4 and forms the $3\text{CaO} \cdot 2\text{SiO}_2$ compound. At 30% of ferrosilicon, another new phase was presented in the residue, the $\text{Ca}_3\text{MgSi}_2\text{O}_8$ compound.

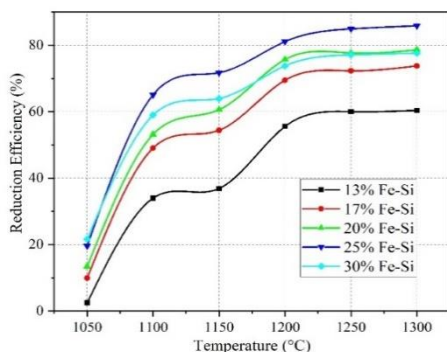


Fig. 6 Effect of temperature on reduction efficiency

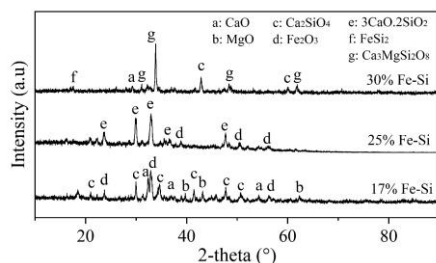
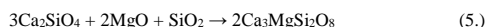


Fig. 7 XRD patterns of remained briquettes after reduction at 1200 °C for 3 hours

The reaction that lead to the formation of $\text{Ca}_3\text{MgSi}_2\text{O}_8$ compound could be:



As a result, a significant amount of magnesium oxide is reacted with Ca_2SiO_4 and trapped in the residue after reduction. The formation of $\text{Ca}_3\text{MgSi}_2\text{O}_8$ causes a loss in MgO and hampered reduction efficiency. $\text{Ca}_3\text{MgSi}_2\text{O}_8$ formation after reduction was also reported in the literature [18, 21].

Effect of CaO/MgO ratio

As discussed above, CaO played a very important role in the reduction of dolomite. CaO and MgO have been added to modifies the CaO/MgO ratio (wt. ratio) in calcined dolomite and study its effect on reduction. **Fig. 8** shows the variation of reduction efficiency when CaO/MgO ratio varied. These specimens have been reduced with 17% ferrosilicon at 1200 °C for three hours.

With the CaO/MgO ratio increases from 1.1 to 1.6, the reduction efficiency increased from 52.2 to 71.3%. After that, it

decreases to 69.6% when the CaO/MgO ratio reached 1.8. The increasing of CaO content might leads to the formation of more Ca_2SiO_4 . The results are in agreement with a previous report in which dolomite was reduced in the Ar atmosphere [18]. Calcinated Thanh Hoa dolomite has the CaO/MgO ratio of approx. 1.51, based on the experimental results there is not necessary to provide additional CaO into the raw material.

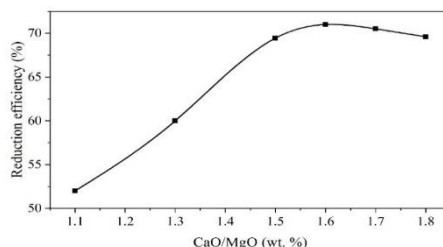


Fig. 8 Effect of CaO/MgO ratio on reduction efficiency

The magnesium product

Fig. 9a shows the magnesium crown crystallized in the cooling area of the reduction retort and **Fig. 9b** is an SEM image of the magnesium crown.

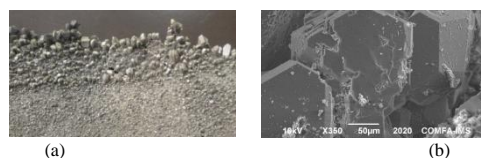


Fig. 9 (a) Magnesium crystallized and (b) SEM image of the magnesium

Small impurities were found on the surface of the magnesium crystals. Chemical analysis revealed the purity of magnesium was from 97.01 to 99.33%. **Fig. 10** shows the XRD pattern of the obtained magnesium crown.

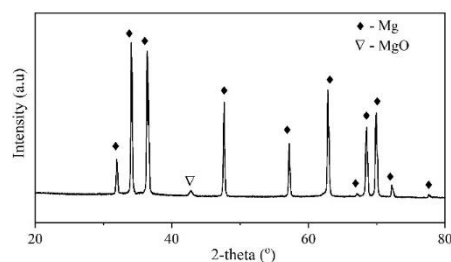


Fig. 10 XRD patterns of the obtained magnesium crown

The XRD pattern reaffirmed that the product was largely containing magnesium metal, the impurity detected by the XRD was MgO . The results indicated that the reduction of calcinated Thanh Hoa dolomite was a success and produced high purity magnesium.

CONCLUSION

Thermodynamic and experimental studies were carried out on the reduction process of Thanh Hoa dolomite to produce magnesium. Thermodynamic calculation pointed out that at a vacuum pressure of 600 Pa, the reduction temperature could be

as low as 1140 °C. Experiment results indicated that although reduction could be done at 1150 °C, the process efficiency was low, generally below 20%. Process efficiency enhanced as temperature increase and reaches the highest value of 85,8% at 1250 °C (25 wt.% ferrosilicons). The amount of ferrosilicon used also has influenced the process efficiency. After three hours of reduction, the obtained magnesium was very high in purity, 99,3%. Theoretically and experimental studies have indicated the feasibility of producing magnesium from Thanh Hoa dolomite.

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