

Magnesium Reduction from Thanhhoa Dolomite by Ferrosilicon and Ferro-Silicocalcium as Reducing Agent

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Abstract— In this paper, a new reducing agent known as ferro-silicocalcium is being studied for its application in magnesium production through the Pidgeon process. Ferro-silicocalcium with main phase components CaSi_2 and Si can reduce Mg from dolomite at a lower temperature than a traditional reducing agent. It thus improves the efficiency of magnesium production and solves the large energy consumption problem of the Pidgeon process. This paper presents thermodynamics calculations and experimental study on reducing magnesium from Thanhhoa dolomite with the new reducing agents known as ferro-silicocalcium and ferrosilicon as traditional reducing agents. From the thermodynamics calculations, CaSi_2 in the ferro-silicocalcium can eliminate magnesium oxide at temperatures 1000°C lower than FeSi_2 in ferrosilicon. This leads to a substantial decrease in the recovery temperature. When CaSi_2 is decomposed, it releases silicon to improve the reduction process at temperatures greater than 1100°C . Experiments are performed to confirm the calculation results. The reduction process of dolomite by ferro-silicocalcium and ferrosilicon was analyzed by phases analysis of reduction slag through X-ray diffraction. The experimental results show that when using ferro-silicocalcium as a reducing agent, the recovering magnesium oxide efficiency reaches 91.3% over three hours with a recovering temperature of 1200°C . The efficiency is 7% higher than the traditional method using ferrosilicon under the same conditions. This proves that using ferro-silicocalcium as a reducing agent reduces the operating temperature of the reducing system and saves energy for the whole process. Therefore, ferro-silicocalcium promises to be an effective alternative reducing agent in magnesium production.

Keywords— Magnesium; Thanhhoa dolomite; thermodynamic analysis; Pidgeon process.

Manuscript received 25 Mar. 2021; revised 14 Jun. 2021; accepted 11 Oct. 2021. Date of publication 30 Apr. 2022.
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I. INTRODUCTION

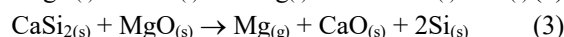
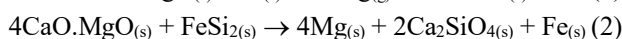
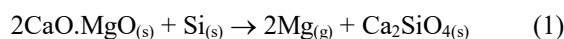
The very large demand for magnesium and Mg alloys in the automotive, biomedicine, mechanical, and mechatronics industries has promoted the research and production of magnesium processes in recent years [1]–[4]. Due to advantages such as ease of practice, the low requirement in the high-quality labor force, flexibility, and an easily adjusted manufacturing process, the Pidgeon procedure invented by Canadian scientist Dr. L.M. Pidgeon is popularly applied to produce magnesium [5]. Currently, the amount of magnesium produced in China occupies 80% of the whole world, and 70% of this amount has been created by Pidgeon [6]. However, in comparison with other methods, the Pidgeon method has low efficiency and wastes energy. An energy-wasting process also creates the reaction substance ferrosilicon of this procedure. Thus, the global warming risk of Pidgeon's method is 50% higher than that of aluminum and steel [7].

There are various improvements for Pidgeon's method to reduce energy consumption and ferrosilicon usage. In particular, the energy consumption efficiency has improved substantially by using microwaves or lasers [8], [9]. Although there is development, this procedure still consumes 11 tons of dolomite, 1 ton of ferrosilicon for each magnesium tone, and exhausts 26 tons of CO_2 and 5.5 tons of slag [10]. The low recovery efficiency leads to high ferrosilicon consumption being the main problem of the Pidgeon procedure. As in many studies, the most important thing is that silicon in ferrosilicon exists in silicon and the FeSi_2 phase. The lowest reacting temperature of silicon and magnesium oxide is approximately 1000°C under vacuum conditions; however, FeSi_2 is higher. Thus, some FeSi_2 phases cannot join in the reaction at a low temperature, or the recovering temperature increases to promote the ferrosilicon reaction. This leads to the low reducing ability of MgO or wastes more energy.

Some researchers have used carbon or CaC_2 as a reducing agent instead of ferrosilicon to reduce the manufacturing cost

and save energy. Although the price of carbon and CaC_2 is half that of ferrosilicon, its efficiency is fairly low [11]–[14]. From the results of using Al powder or Al-Si compounds, these reducing agents can decrease the procedure temperature [15]–[17]. The Al-Si compound has a high cost, so it is difficult to use it in manufacturing. Meanwhile, Ca-Si exhibits benefits and has a similar price as ferrosilicon and noticeable greater productivity.

Dolomite is a crucial raw material in magnesium production by the silicothermic method with the main ingredient of $\text{CaCO}_3\text{-MgCO}_3$. According to the Vietnam Environmental Resources Ministry, there is a very large dolomite reserve with 1.5 billion tons. However, there are no factories producing magnesium, while domestic industries' magnesium and magnesium alloy demand increase rapidly. This paper implements magnesium recovery from Thanhhoa dolomite ore under vacuum conditions by the Pidgeon method. The possibility of this recovery method has been approved by a thermodynamic analysis using ferrosilicon and ferro-silicocalcium as reducing agents. The reactions between Thanhhoa dolomite and ferrosilicon are shown in formulas (1) and (2), whereas the main reactions with ferro-silicocalcium are shown in formulas (1) and (3):



The ferro-silicocalcium compound mostly includes calcium and silicon in two phases, Si and CaSi_2 . Like ferrosilicon, ferro-silicocalcium is a popular alloy in the steel industry. Although its price is now higher than that of Fe-Si, its advantages in magnesium recovery efficiency make it a common reducing agent.

II. MATERIALS AND METHODS

A. Materials

The dolomite sample in the experiment is collected from Thanhhoa mines in the middle of Vietnam. After heating the dolomite at 1100°C for approximately three hours (dolime), the ingredients were analyzed as shown in Table 1 and Fig. 1. Chinese ferrosilicon and ferro-silicocalcium have the ingredients shown in Table 1.

TABLE I
THE MAIN INGREDIENTS OF THANHHOA DOLIME, FERROSILICON AND FERRO-SILICOCALCIUM

| Thanhhoa dolime | | | | |
|---------------------|----------------|-------------------------|-------|-------|
| Composition, | SiO_2 | Fe_2O_3 | MgO | CaO |
| wt (%) | 0.30 | 0.15 | 37.28 | 54.80 |
| Ferrosilicon | | | | |
| Composition, | Si | Fe | C | P |
| wt (%) | 72.00 | 27.00 | 0.10 | 0.03 |
| Ferro-silicocalcium | | | | |
| Composition, | Ca | Si | Fe | Al |
| wt (%) | 31.30 | 61.20 | 3.12 | 2.40 |

After the heating step, the dolomite was ground into particles with dimensions less than $100\ \mu\text{m}$ before mixing the dolomite particles with the ferrosilicon and ferro-

silicocalcium powders with catalyst CaF_2 . Then, the mixture was compressed by a hydraulic into cylinder briquettes with a diameter of 15 mm, the height of 20 mm, and compressing force of 60 MPa. The recovering equipment was employed in this procedure with a stainless-steel tube for 310s, which is often called the retort (Fig. 2). Its diameter was 65 mm, and its length was 1100 mm. The retort was heated by using silicon carbide heating elements with a maximum temperature of 1300°C allocated inside the furnace.

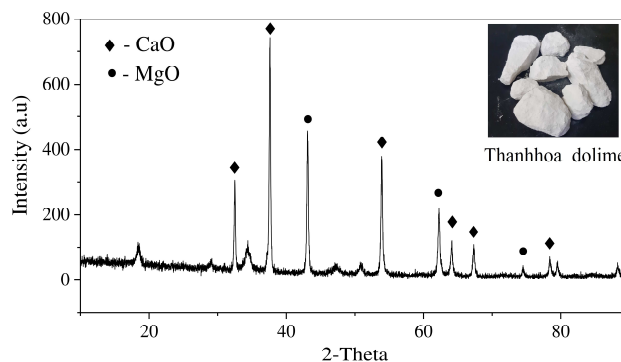


Fig. 1 XRD pattern Thanhhoa Dolomite after calcination



Fig. 2 The experimental furnace

The head of the retort was connected to the vacuum pumping system, including a two-stage vacuum pump, pressure sensor, and shut-off valve. The rest was linked to the argon gas system. Thermocouples were employed to measure and control the temperature in the reacting area and cooling space where the magnesium crystallized. The temperature and pressure were two important factors for this procedure, so they were continuously recorded throughout this process. The circulating liquid was used to keep the furnace entrance at $600\text{-}700\ ^\circ\text{C}$ to obtain the magnesium.

B. Methods of the Experiment

1) *Thermodynamic Calculation.* The thermodynamic analyses among the reactions related to the reducing dolomite process with reducing agents such as ferrosilicon and ferro-silicocalcium are performed by arranging the Gibbs free energy. The results are similar to those obtained by the temperature diagram ($\Delta G - T$) using FactSage 7.2 software.

This kind of software is based on the FactPs FToxid và FTSalt database [18].

2) *Verification Tests*. Experiments using different kinds of reducing agents are performed to verify the thermodynamic results. They are performed with the mixture in the form of briquettes. These briquettes are formed by the furnace, as shown in Figure 3. Based on the experimental data for dolomite Thanhhoa [19], the mixture has an ingredient of 72% dolomite, 25% reducing agent, and 3% catalyst CaF_2 with a mixture mass in each experiment of 250 g. The briquettes are arranged horizontally in the furnace with a vacuum of 100 Pa before heating to 700 °C, and they are kept at this temperature level for one hour to eliminate the water and carbon dioxide residue in the briquettes. Then, the reducing temperature continues to increase for 3 hours. The general flowchart of reducing magnesium from Thanhhoa dolomite ore is shown in Fig. 3.

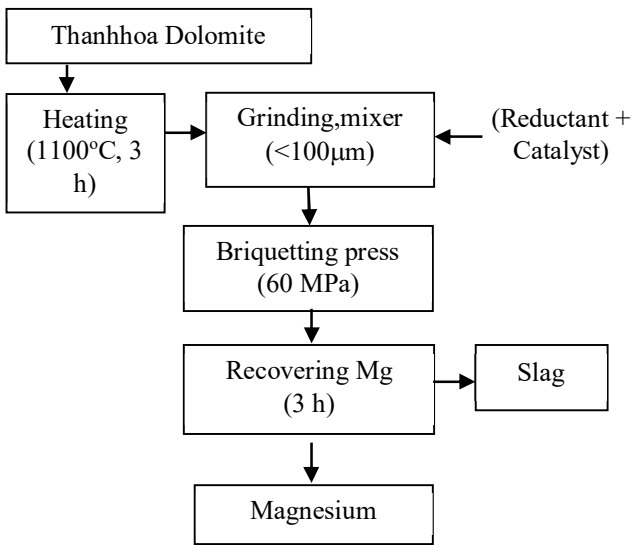


Fig. 3 Mg production process diagram

After the reducing process, the waste and product are removed for analysis, and the amount of magnesium before and after the process is measured to calculate the reducing efficiency as:

$$\text{Recovery Efficiency} = \frac{w_1 \times m_1}{w_2 \times m_2} \quad (4)$$

Where:

- m_1 is the mass of the condensed magnesium, w_1 is the weight fraction of magnesium in the condensed magnesium.
- m_2 is the mass of the briquette residues before reduction and w_2 is the weight fraction of magnesium in the briquette before reduction.

The chemical compositions of dolomite and magnesium were measured by an X-ray fluorescence (XRF) spectrometer Bruker S4– Pioneer. To identify the phase changes in the briquettes after vacuum recovery, the phase compositions are determined EQUINOX 5000 (Thermo Scientific, France) X-ray diffraction spectroscopy the SEM images of the magnesium crown by SEM JEOL Model JSM-6490.

III. RESULT AND DISCUSSION

A. Thermodynamic Analysis

In terms of the magnesium recovery performed by the silicothermic method under vacuum conditions, the reducing agent, pressure, and temperature reaction play an important role in the process. Thus, it is necessary to analyze the reactions among the dolomite and reducing agents such as Si, FeSi_2 , and CaSi_2 to determine the most suitable reaction for magnesium recovery. According to the dolomite compositions, the possible reactions among the magnesium oxide and reducing agents are given by equations (1), (2), (3).

The database from the FactSage software is implemented to calculate the relationship between ΔG -T in each reaction under different vacuum conditions. The initial calculated temperature is under 50°C in comparison with the melting temperature of magnesium. The balanced vapor pressure of magnesium PMg is nearly equal to the residual pressure in the system. The free energy calculation method Gibbs in the vacuum condition according to the Vant't Hoff equation is demonstrated in formula (5).

$$\Delta G = \Delta G_0 + RT \ln K_P \quad (5)$$

For the dolomite reducing reaction with Si:

$$K_P = \frac{(P_{\text{Mg}}^2 \cdot \alpha_{\text{Ca}_2\text{SiO}_4})}{(P_0^2 \cdot \alpha_{\text{CaO}}^2 \cdot \alpha_{\text{MgO}} \cdot \alpha_{\text{Si}})} \quad (6)$$

For the dolomite reducing reaction with FeSi_2 :

$$K_P = \frac{(P_{\text{Mg}}^4 \cdot \alpha_{\text{Ca}_2\text{SiO}_4} \cdot \alpha_{\text{Fe}})}{(P_0^4 \cdot \alpha_{\text{CaO}}^4 \cdot \alpha_{\text{MgO}}^4 \cdot \alpha_{\text{FeSi}_2})} \quad (7)$$

For the dolomite reducing reaction with CaSi_2 :

$$K_P = \frac{(P_{\text{Mg}}^2 \cdot \alpha_{\text{CaO}} \cdot \alpha_{\text{Si}}^2)}{(P_0^2 \cdot \alpha_{\text{CaSi}_2} \cdot \alpha_{\text{MgO}})} \quad (8)$$

Where:

- ΔG : the Gibbs free energy at a partial pressure in the system
- ΔG_0 : the Gibbs free energy at atmospheric pressure
- PMg: the partial pressure of magnesium vapor in the reduction retort
- P_0 : the atmosphere pressure is 101325 Pa
- α_{CaO} , α_{MgO} , α_{Si} , α_{FeSi_2} , and α_{CaSi_2} are the activity of CaO, MgO, Si, FeSi_2 , and CaSi_2 , respectively. They are nearly equal to 1.

The calculation for the ΔG -T diagram of the reactions is shown in Fig. 4. As shown in Figure 4.a each pressure level will have its temperature to make the phase Si react with the magnesium in the dolomite to create magnesium gas. At atmospheric pressure (100 000 Pa), the process requires a reaction temperature higher than 1480°C (Gibbs free energy: $\Delta G > 0$). However, the minimum temperature for the recovery process decreases substantially in the vacuum environment. When the system pressure decreases to 700 Pa, the minimum temperature decreases to 1060°C and decreases to 960 °C at 100 Pa.

When the magnesium oxide in the dolomite reacts with the FeSi_2 residue in the ferrosilicon, the ΔG value of the reaction between MgO and FeSi_2 noticeably decreases with increasing temperature and pressure, as shown in Fig. 4.b. The minimum temperature for the recovery process at atmospheric pressure is 1580 °C. When the pressure decreases to 700 Pa and 100 Pa, the minimum temperatures are 1160 °C and 1040 °C, respectively. The minimum temperature for the magnesium to react with FeSi_2 is higher than that with Si. Thus, with the composition of 54.8% Si and 41.7% FeSi_2 , at temperatures

under 1100 °C, mostly phase Si joins in the reaction. This leads to the limit of the recovery efficiency, but when the temperature increases to 1160°C, the phase FeSi₂ is present as well. At this point, the efficiency increases rapidly. This finding is suitable compared with the practical results of previous studies [20].

In terms of the CaSi₂ reaction in ferro-silicocalcium, MgO is reduced into Mg(g) at 1620 °C with atmospheric pressure (Fig. 4.c). When the system pressure decreases to 700 Pa and 100 Pa, the temperature decreases to 1000 °C and 960 °C, respectively.

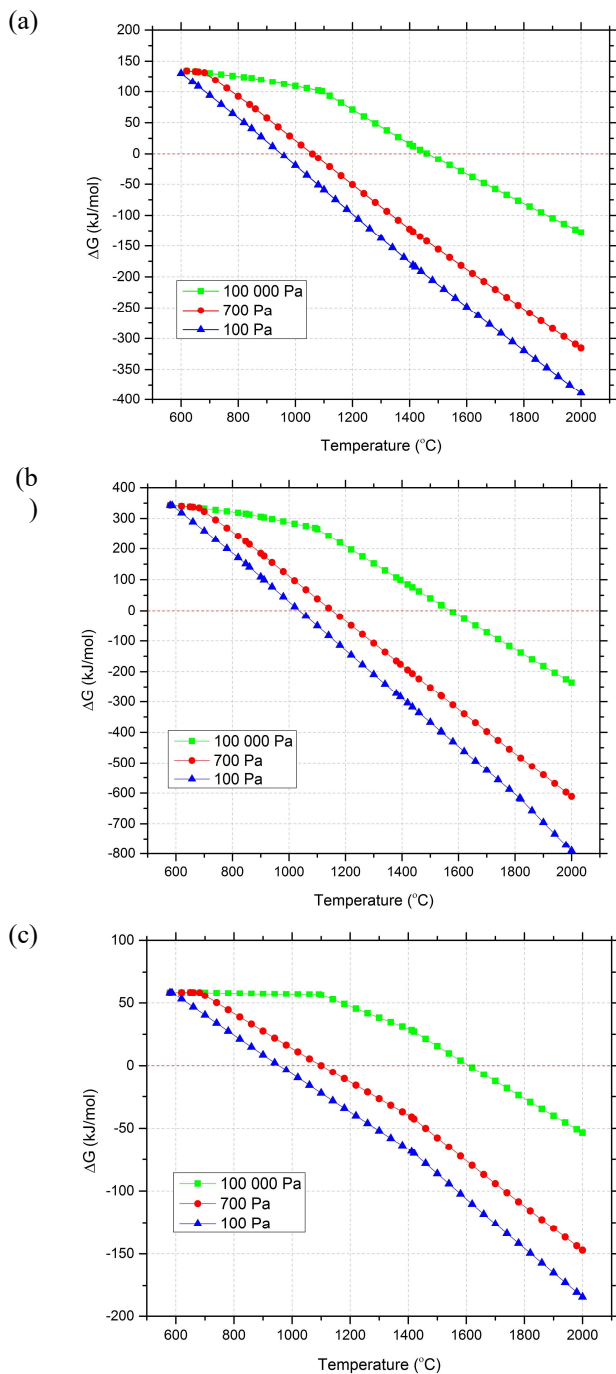


Fig. 4 ΔG -T diagram for the reactions between MgO and (a) Si, (b) FeSi₂, and (c) CaSi₂

The balance stages and the changes in the main phases corresponding to the increase in temperature in the range of 500-1400 °C are calculated for reducing magnesium from dolomite by using the combination of Fe-Si and Ca-Si as reducing agents. The calculation results are shown in Fig. 5. These diagrams are computed with the amount of reducing agent equal to 100% of the amount of chemical equilibrium at 100 Pa.

The main phases in the product of the reaction with Fe-Si are Ca₂SiO₄ and Mg v̄ a little Fe (Fig. 5.a). When the temperature is over 1200 °C, the appearance of Ca₃MgSi₂O₈ (merwinite) causes the amount of Mg in the combination to be stuck in the slag, so the process efficiency is not able to increase. Merwinite tends to decompose when the temperature reaches 1400 °C; however, at this point, there is an amount of Ca with high purity. Thus, the ideal recovery temperature for the process with ferrosilicon as the reducing agent should be in the range from 1150 °C to 1250 °C. Phases such as Ca₂SiO₄ and Mg exist in the final products when Ca-Si is used as a reducing agent (Fig. 5.b). Moreover, Ca appears at temperatures under 1200°C, and the existence of aluminum in the ferro-silicocalcium leads to the creation of phase Ca₃Al₂O₆. In this case, the mass of magnesium in the gas form will reach the maximum value and be stable at temperatures higher than 1100 °C, while with the application of Fe-Si, the maximum magnesium will be obtained at temperatures over 1400 °C. This leads to the estimation of higher production efficiency and lower process temperature if ferro-silicocalcium is applied, saving the process energy consumption and improving the duration of the equipment.

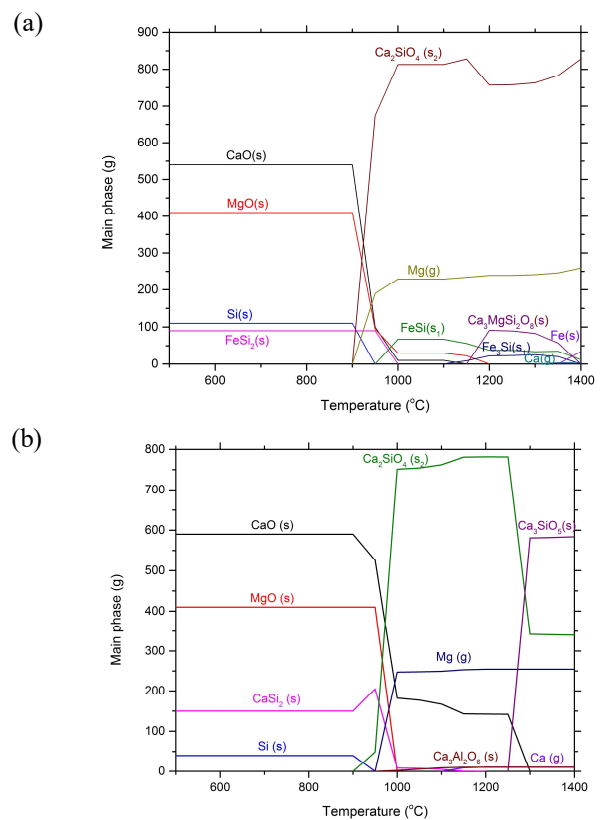


Fig. 5 The change in the main phases for different reductant types at 100 Pa Fe-Si and (b) Ca-Si

According to the above analysis, the magnesium recovery procedure of dolomite from Thanhhoa requires a high temperature for the reaction at atmospheric pressure; however, the minimum temperature could decrease substantially by decreasing the system pressure. Comparing the two phases CaSi_2 and FeSi_2 , the former requires a lower magnesium recovery temperature than the latter, especially under vacuum conditions. Thus, unlike the process using ferrosilicon as a reducing agent, although the silicon in the ferro-silicocalcium exists in the form of a compound such as CaSi_2 , it joins in the reducing reactions at low temperatures and releases the silicon molecules before continuing the recovery reaction at higher temperatures, especially when the system pressure is below 100 Pa. Moreover, Ca-Si-Fe in the ferro-silicocalcium creates a low melting ternary with a melting point lower than ferrosilicon. This produces all kinds of reducing agents spread on the oxide molecules' surfaces, so the recovery reaction is now a liquid-solid reaction at low temperatures. This is the reason for the rapidly proceeding reaction.

B. Results of the Verification Test

To verify the thermodynamic results, recovery experiments in a vacuum environment are performed with Fe-Si and Ca-Si with two reducing agents. The efficiency of reducing the magnesium process is shown in Fig. 6. The results illustrate that the ideal process efficiency will reach a Ca-Si rate of more than 91% at 1200 °C for 3 hours. Its efficiency is 6.7% higher than using Fe-Si under the same conditions. This means that applying Ca-Si for recovering magnesium from Thanhhoa dolomite achieves better improvement than Fe-Si. Ca-Si is suitable for the thermodynamic results. The effective ferro-silicocalcium application is clearest at temperatures from 1000 °C to 1100 °C.

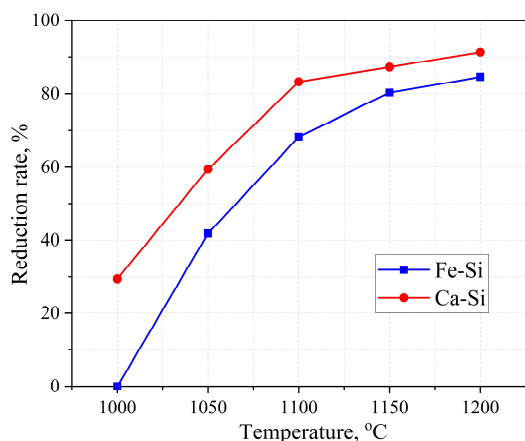


Fig. 6 Effect of the temperature on the recovery efficiency with Fe-Si, Ca-Si as reducing agent

In this temperature range, the process efficiency using ferro-silicocalcium is substantially higher (17%) than that using ferrosilicon. Meanwhile, in the range from 1150 to 1200 °C, the distance decreases by 6-7%. The thermodynamics view can explain this issue that CaSi_2 is able to react with MgO at temperatures under 1000 °C completely. After that, the temperature increases over 1000 °C, silicon starts joining in the reducing reactions, so the efficiency increases quickly, while at this temperature, FeSi_2 in ferrosilicon does not react. At temperatures above 1100 °C, especially 1150-1200 °C, FeSi_2 starts joining in the

recovering reaction, and the gap decreases. Therefore, at the temperature of 1000 °C, it can be seen that metallic magnesium cannot be recovered when using ferrosilicon reducing agent.

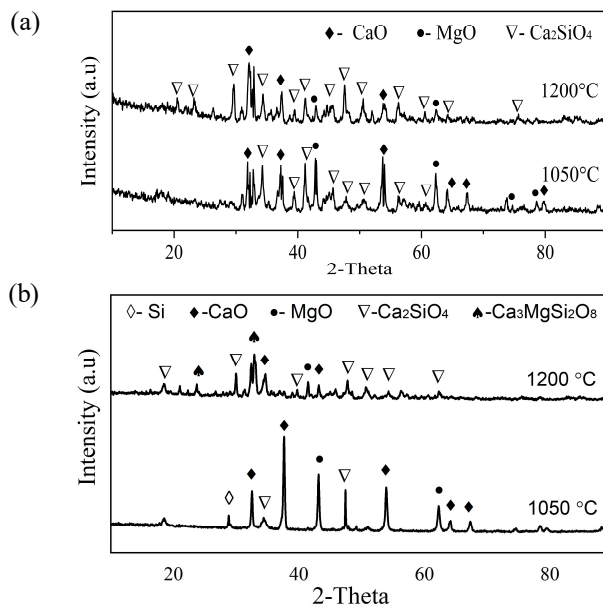


Fig. 7 XRD patterns of slag: (a) Ca-Si, (b) Fe-Si

Fig. 7 shows the stages of the slag after the recovery process with the phase changes in the rest of the briquettes. Regarding ferro-silicocalcium, in the slag at 1050 °C, the main phase is CaO-MgO , which does not react, and Ca_2SiO_4 . This proves that CaSi_2 has reacted completely, and Si begins reacting to create calcium silicate. Ferrosilicon has not yet reacted at this temperature and exists in the slag. While at 1200 °C, with Fe-Si reducing agent, the presence of $\text{Ca}_3\text{MgSi}_2\text{O}_8$ phase in the briquette residues after reduction caused Mg to be trapped in the waste resulting in lower efficiency. The residue using Ca-Si reducing agent is mainly the calcium silicate phase.

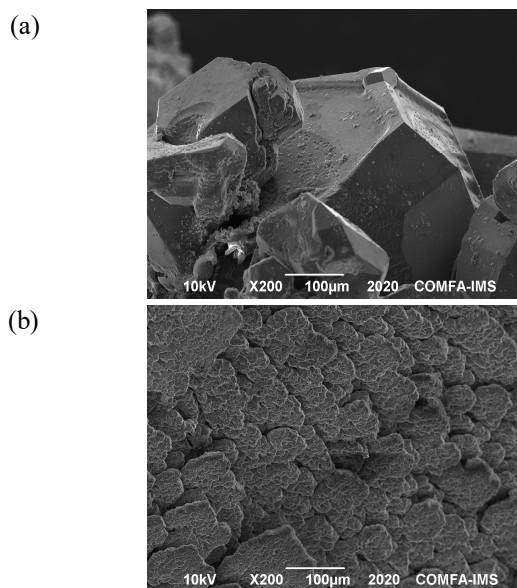


Fig. 8 SEM image of the Mg crown in the head (a) and the rear (b) of the cooling space from the experiment using reducing agent Fe-Si

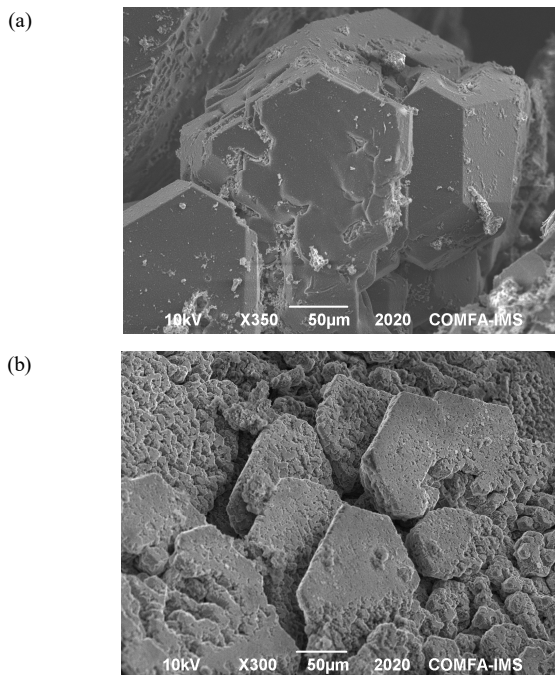


Fig. 9 SEM image of the Mg crown in the head (a) and the rear (b) of the cooling space from the experiment using reducing agent Ca-Si

Chemical composition analysis of the Mg crown indicates that the impurities are not considerably different in the two cases, and the pureness is higher than that of the magnesium crown in the experiments using carbon or Al-C powder [13], [21]. The purity of magnesium crown when using Fe-Si and Ca-Si reducing agents is 99.3 % and 98.8 %, respectively.

The SEM images of the magnesium crown from the experiment using JEOL Model JSM-6490 are shown in Fig. 8 and Fig. 9. The products in both situations have an irregular shape with a compact structure and good crystallization ability. The head of the cooling space has a temperature over 700 °C, and there is the existence of highly pure crystal magnesium with the hexagonal structure, while the rear cooling space has low crystalline magnesium deposition at approximately 600 °C. The appearance of impurities is recorded in this space. The application of reducing agents such as Fe-Si or Ca-Si will reach a high purity, so the later refining process has no high requirement, as in the case of implementing carbon or CaC₂, which is always refined by vacuum distillation with costly production.

IV. CONCLUSION

The efficiency of the magnesium recovery process from dolomite of Thanhhoa by using ferro-silicocalcium is verified based on the results from thermodynamic analyses and experiments. The thermodynamic results from FactSage software indicate that MgO in the dolomite can be reduced at temperatures under 1000 °C by Ca-Si with a pressure of 100 Pa. For the reducing agent Ca-Si and Fe-Si, there are two recovery periods. The first period is when the CaSi₂ in ferro-silicocalcium is present in the MgO reducing reaction and releases the Si molecule. The second is when the silicon in the compound and released silicon in the first period are in the reaction. With the reducing agent Fe-Si, the first period is when the reaction between MgO and Si occurs, and the second period is when FeSi₂ eliminates MgO at over 1100 °C.

The required temperature in the silicocalcium case is lower than that in the other case so the energy cost will decrease.

The experiment has shown that if the recovery process is performed at 1200 °C for 3 hours with 72% dolomite, 25% reducing agent, and 3% catalyst (CaF₂) at 100 Pa, the magnesium recovery efficiency is 91.3% for Ca-Si and 84.6% for Fe-Si. The quality of the crystallized magnesium in the two cases does not substantially differ, with high purities of 99.3 % and 98.8 %.

ACKNOWLEDGMENT

This study was supported by the Experimental Center – Vietnam Maritime University and School of Materials Science and Engineering – Hanoi University of Science and Technology.

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