EFFECTS OF BRIQUETTING PRESSURE ON THE VACUUM THERMAL REDUCTION OF MAGNESIA BY ALUMINUM AT 1200°C

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Abstract

Aluminothermic reduction of magnesia under vacuum condition has been proved to be an effective way to extract magnesium from dolomite and magnesite. This thermal reduction process involves solid, liquid and vapour phases and the briquette preparation condition has a great influence on the extent of the reactions. In this paper, the effects of briquetting pressure, ranging from 10 MPa to 250 MPa, on the vacuum thermal reduction of magnesia by aluminum at 1200°C were investigated. The variations of the reduction ratio of magnesia, the phase constitution as well as morphology of the briquette residues, with the changes in the briquetting pressure, were studied via X-ray diffraction analysis, scanning electron microscopy and energy dispersive spectrometry. It was revealed that the reduction ratio of magnesia increased with the increase in the briquetting pressure. The briquette residues show a whitish core and the grayish outer shell. The core part mainly contains the spinel phase and unreacted magnesia phase, which does not change with the briquetting pressure. The phases presented in the outer shell of the briquette residues vary greatly with the briquetting pressure. At lower pressure such as 10 MPa and 50 MPa, the major phases are spinel, the MAO (magnesium aluminum oxide), unreacted magnesia and aluminum, while at high pressure 100 MPa to 250 MPa, the major phases are α-alumina, MAO and unreacted aluminum.

Keywords: Aluminothermic reduction, magnesia, briquetting pressure, magnesium.

1. INTRODUCTION

Magnesium is one of the lightest structural materials with a density of 1.74 g/cm^3, only 65% of that of aluminum and 22% of that of iron [1]. Commercially magnesium is produced by two processes, electrolysis of molten magnesium chloride and the Pidgeon process, a thermal reduction process using calcined dolomite as raw material and ferrosilicon as the reducing agent. At present, primary magnesium in China is mainly produced by the Pidgeon process. However, the Pidgeon process has demerits of the low efficiency of energy consumption and resources usages as well as serious environmental pollution.

Recently, Ma and his colleagues developed a new process to produce primary magnesium using dolomite ores as the raw material [2-3]. In this process, the magnesia component and calcia component in the dolomite are firstly separated. Then the magnesia is used to produce primary magnesium by aluminothermic or carbothermic reduction under vacuum condition and calcia is used to make calcium carbonate as a co-product. Compared to the Pidgeon process, this process has advantages of higher efficiency of resources usages and energy consumptions, as well as lower amount of solid waste discharge.

Aluminothermic reduction of magnesia under vacuum condition is a multi-phase chemical reactions, in which the reactant MgO and products spinel, α-alumina are in solid state, the reactant aluminum is in liquid state, and the product magnesium is in vapour state. For the multi-phase chemical reactions, the briquette preparation condition has a great influence on the extent of the reactions. In this paper, the effects of briquetting pressure, ranging from 10MPa to 250MPa, on the vacuum thermal reduction of magnesia by aluminum at 1200°C were investigated, aiming to provide the fundamental understandings of the process and the basis for the improvement of process conditions.

2. EXPERIMENTAL DETAILS

2.1 Materials and experimental process

The raw materials used in this work were the analytical pure magnesia powder and the aluminum powder with the purity of 2N and the particle size of 100-200mesh. The magnesia and aluminum powder, with the MgO to Al molar ratio of 3:2, was first weighted and well mixed, then cold-pressed to the briquettes with the diameter of 40mm and thickness of about 10mm under different briquetting pressures ranging from 10 MPa to 250 MPa. These briquettes were placed in a vacuum retort and heated to 1200 °C and hold for reduction reaction to process. The magnesium vapour formed in the reaction was transferred to the condensed magnesium in the condensing sleeve in the retort. After thermal reduction, the condensed magnesium and the remaining briquette residues were collected and weighted.

The reduction ratio of magnesia (η) is defined as the ratio of briquette mass loss to the initial magnesium mass in the briquette,

$$\eta = \frac{\Delta M}{M_0\ w_{Mg}} 100 = \frac{M_0 - M}{M_0\ w_{Mg}} 100\ [\%] \qquad (1)$$

in which the M_0 and M are the mass of the briquette before and after thermal reduction, respectively. The w_{Mg} is the weight fraction of magnesium in the briquette before thermal reduction.

2.2 Characterization

X-ray diffraction (XRD) analysis was run on a D/max-rA rotating anode X-ray diffractometer equipped with Cu-Kα radiation in the 2θ range of 10 to 90°. Phase identification was made by searching the ICDD powder diffraction file database. Morphology of the condensed magnesium and the briquette residues was investigated on the carbon-coated samples using a ZEISS EV018 scanning electron microscopy (SEM) with an attached Bruker XFlash Detector 5010 energy dispersive spectrometry (EDS) unit.

3. RESULTS AND DISCUSSION

3.1 Effects of briquetting pressure on the reduction ratio of magnesia

In the vacuum aluminothermic reduction of magnesia, the magnesia is reduced to magnesium vapour which condenses to solid magnesium in the condenser region of the vacuum retort. **Fig. 1** shows the effect of briquetting pressure on the reduction ratio of magnesia. The reduction temperature and time were fixed at 1200 °C and 1 hour. The reduction ratio of magnesia increases rapidly from ~73 % to ~82 % when the briquetting pressure increases from 10MPa to 100MPa. Further increases in briquetting pressure from 100 MPa to 200 MPa lead to the minor increase in the reduction ratio of magnesia from ~82 % to ~87 %. Beyond 200MPa, the reduction ratio remains nearly constant.

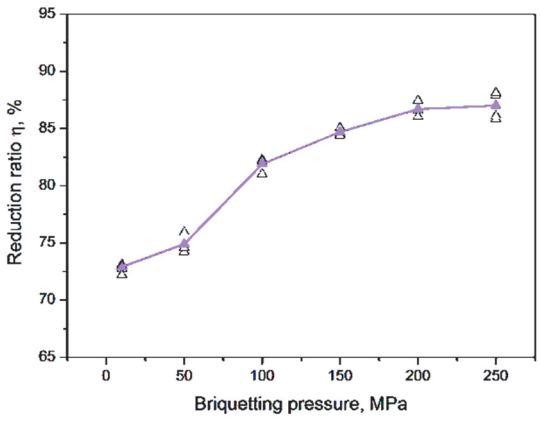


Fig. 1 Effect of the briquetting pressure on the reduction ratio of magnesia

The vacuum aluminothermic reduction of magnesia at 1200 °C is a typical heterogeneous multi-phase reactions, in which the reactant magnesia is in solid state, aluminum in the liquid state while one of the products magnesium in the vapour state. Since the chemical reactions between the reactants MgO and Al occur at the interface of MgO and Al, the contacting area and

angle between MgO and Al play important role in the kinetics of the reaction. Increasing in the briquetting pressure will increase the contact area between magnesia and aluminum, leading to the increase in the reduction ratio of magnesia. Increasing in the briquetting pressure will increase the relative density of the briquette, leading to an increased thermal conductivity, which will speed up the chemical reactions.

3.2 Effects of briquetting pressure on the phase constitution of briquette residues

After thermal reduction, the surface of the briquette residues appears in different colour when the briquetting pressure changes, from pale white (10 and 50 MPa) to grey (100-250 MPa). **Fig. 2** shows the cross-sections of the briquette residues. Obviously, the core and outer shell of the briquette residues look different in colour. The core (the central part) is in white colour and the out-layer is in grey colour, indicating the difference in the phase constitutions in the different positions of the briquette residues.

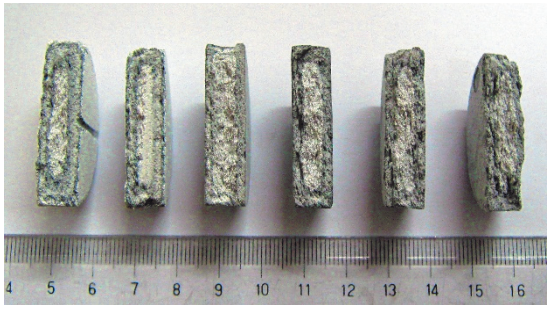


Fig. 2 Photo showing the cross-sections of the briquette residues. From left to right, the briquetting pressures are 10, 50, 100, 150, 200, 250 MPa

Fig. 3 is the X-ray diffraction spectra of samples taken from different positions of the briquette residues, in which the Core refers to the central part, the TRS refers to the transition region between the central part and the outer

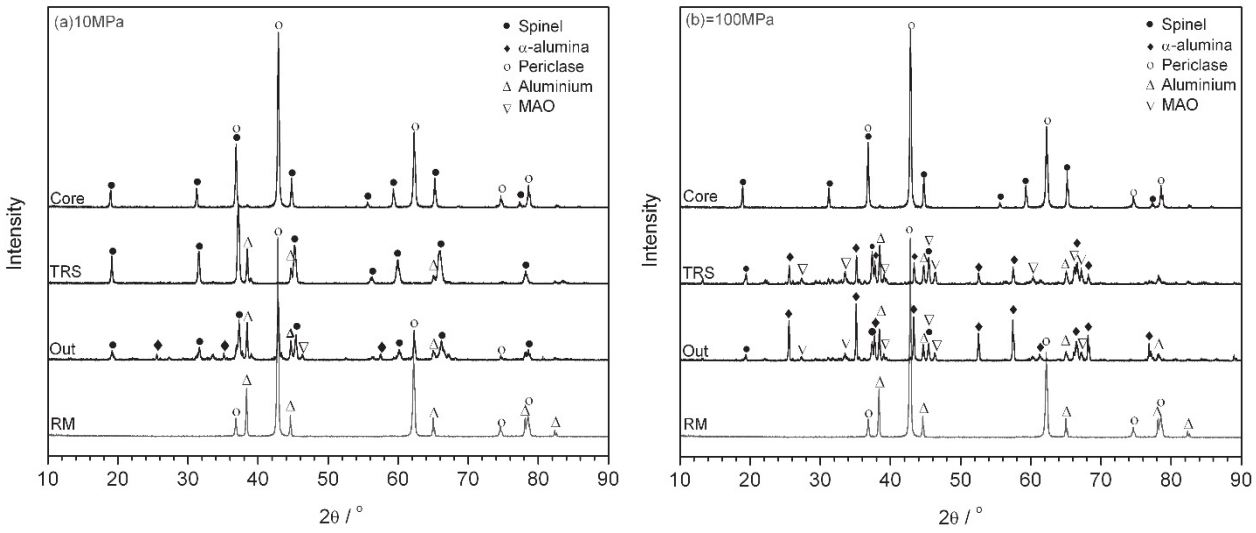
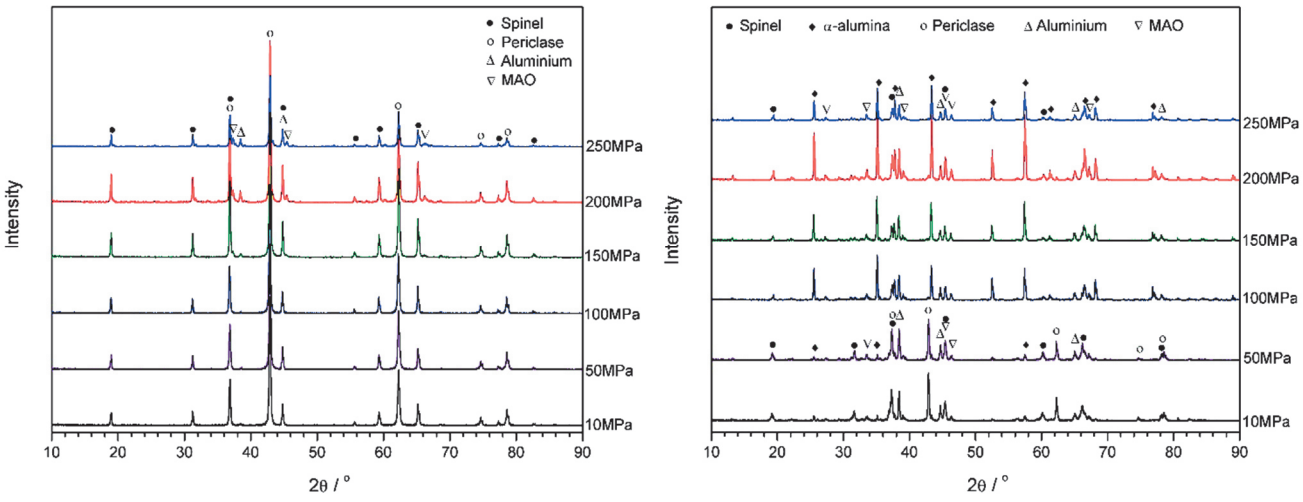


Fig. 3 XRD spectra of the briquette residues. (RM-raw materials mixture, Out-outer shell, TRS-transition region, Core-Central part of the briquette residues)

shell, and the Out represents the outer shell of the briquette residues. The XRD spectra of the briquette before thermal reduction, representing the mixture of raw materials MgO and Al, were superimposed in **Fig. 3** for comparison. The phases presented in the different position of the briquette residues differ greatly. When the briquetting pressure was 10 MPa, the phase changed from spinel, unreacted MgO in the core part, to spinel, unreacted Al in the transition region, to spinel, magnesium aluminum oxide (MAO in short), trace amount of α-alumina, MgO, Al in the outer shell. When the briquetting pressure was 100 MPa, the phases in the core part is similar to that in 10 MPa, but for the phases in the outer shell, the intensity of the diffract peaks for α-alumina is much stronger. The diffraction peak for unreacted MgO was not detected.

In order to compare the effect of briquetting pressure on the phase constitutions of the briquette residues, samples were taken from the similar positions in the briquette residues and analysed by X-ray diffraction. **Fig. 4a** is the XRD spectra for the samples taken from the central part. It could be seen that the major diffraction peaks remain almost unchanged when the briquetting pressure increases from 10 MPa to 250 MPa. The major phases presented are the spinel and unreacted MgO. When the briquetting pressure is around 200 to 250 MPa, small amount of MAO and unreacted aluminum were detected. **Fig. 4b** is the XRD spectra for the samples taken from the outer shell. It could be seen that the briquetting pressure has a great influence on the phase constitutions. When the briquetting pressure is lower, the outer shell of briquette residue mainly contains spinel, MAO and unreacted MgO and Al. Using higher briquetting pressure, large amount of α-alumina was detected.



(a) (b)

Fig. 4 XRD spectra of the briquette residues. (a) the central part; (b) the outer shell

The major chemical reactions occurred during the aluminothermicreduction of magnesia are shown below.

$$4\ MgO(s) + 2\ Al(l) = MgAl_2O_4(s) + 3\ Mg(g) \quad (2)$$

$$3\ MgAl_2O_4(s) + 2\ Al(l) = 4\ Al_2O_3(s) + 3\ Mg(g) \quad (3)$$

The enthalpy changes for reactions (2) and (3) at 1200 °C are 508 kJ and 546 kJ, respectively. That means that both reactions are endothermic. Heat is needed to keep the reactions going right. The chemical reaction starts at the surface of the briquette. As the reaction proceeds, the aluminum near the surface is consumed to form spinel and alumina. The liquid aluminum may transfer from the central part of the briquette to the outer shell, leading to central core lean in aluminum and outer shell rich in aluminum, which was proved by out former work [4].

It is well known that the briquetting pressure affects the properties of briquettes, the higher the briquetting pressure, the larger contact area between MgO and Al, the higher the packing density and the higher the thermal conductivity. At lower briquetting pressure such as 10 MPa and 50 MPa, the liquid aluminum can transfer to the outer shell more easily, but the contact area between MgO and Al is smaller, leading to a slower reaction rate. At the same time, low thermal conductivity impedes the heat transfer from surface to the central core of the briquette. Therefore, the reaction ratio of magnesia is lower for 10 MPa and 50 MPa. Even at the outer shell of the briquette, the amount of α-alumina is negligible.

When the briquetting pressure increased to 100 MPa and larger, the contact area between MgO and Al increased and the reaction rate increased. Large amount of α-alumina was detected at the outer shell. When

the briquetting pressure is 200 MPa and 250 MPa, the transfer of liquid aluminum from central core to the surface might become slower due to the high packing density, small amount of un-reacted Al was detected. Trace amount of the intermediate compound MAO was formed in the central core since heat could transfer easily due to the high thermal conductivity. Too high briquetting pressure may cause the escaping of magnesium vapour to the surroundings more difficult, limiting the further increases in the reduction ratio of magnesia.

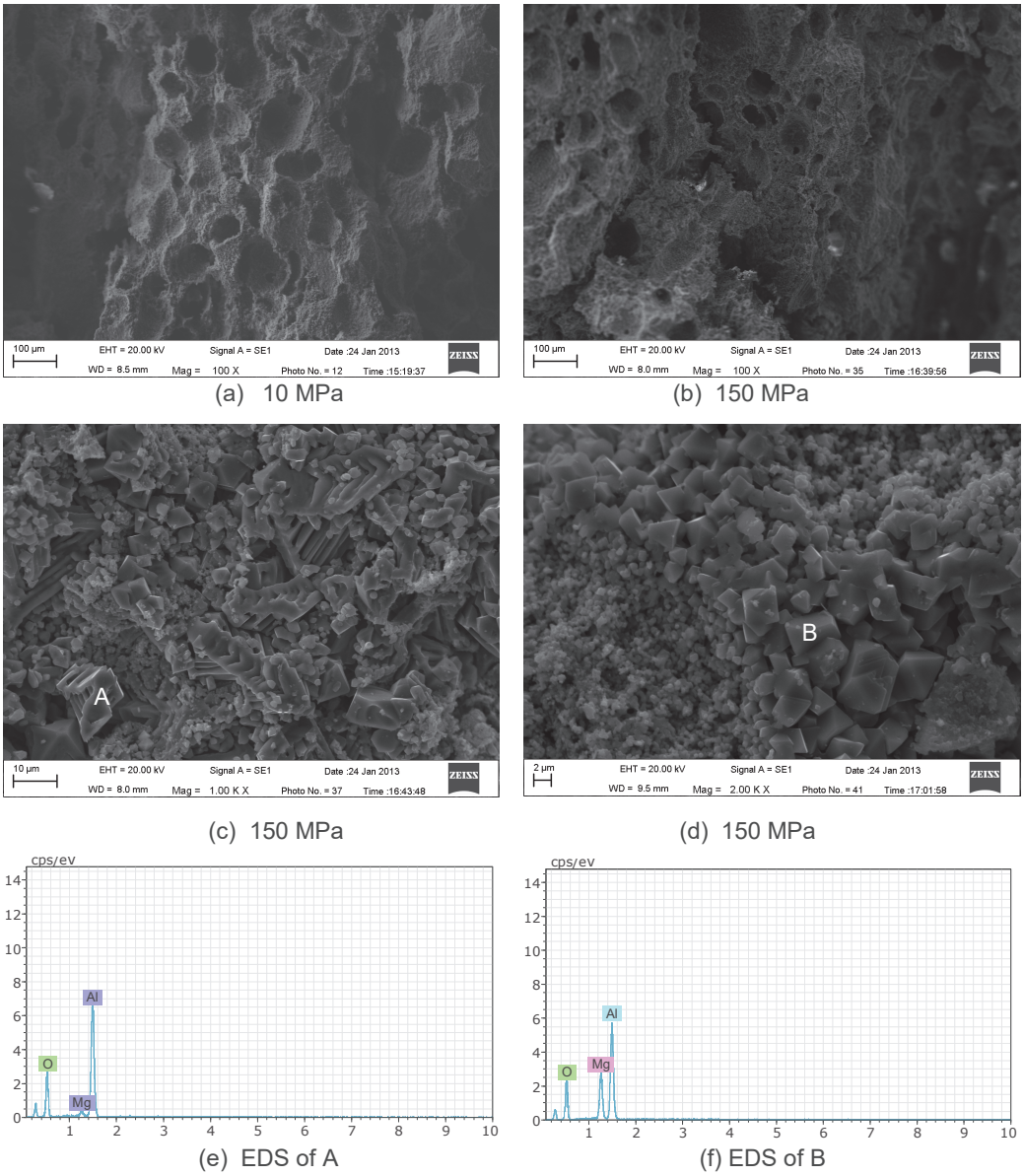


Fig. 5 SEM micrograph shows the morphology of the briquette residues after thermal reduction at 1200°C for 1 hour and the analysis of composition by EDS.

Fig. 5 shows the morphology of the briquette residues after 1 hour thermal reduction at 1200°C when the briquetting pressure varies. Generally speaking, the microstructure of the briquette residues is heterogeneous. As shown in **Figs. 5a** and **5b**, the spherical concaves, which can be seen under lower magnification SEM image, are formed when the pressure inside the Mg vapour bubbles increases and then escapes to the surface of the briquettes. Changing in the briquetting pressure does not show great influences on the heterogeneous

nature of the microstructure. **Figs. 5c** and **5d** are the SEM micrographs taken at higher magnification. The detailed microstructure of the briquette residues changes from place to place and particles with different morphology coexist in the same briquette residue. **Fig. 5e** is the EDS analysis of A marked particle in the **Fig. 5c**, which has a composition of alumina. **Fig. 5f** is the EDS analysis of B marked particle in the **Fig. 5d**, which has a composition of spinel.

CONCLUSION

The influences of briquetting pressure, ranging from 10MPa to 250MPa, on the vacuum thermal reduction of magnesia by aluminum at 1200°C were studied. The reduction ratio increased obviously with the increase in briquetting pressure when the reaction time was fixed to 1 hour with the MgO to Al molar ratio of 3:2.

The obtained briquette residues were heterogeneous and the phase constitutions in the outer shell and the central core differed greatly. The briquetting pressure showed minor influence on the phase constitutions in the central core, but had a large influence on that of the outer shell. The central core mainly contained the spinel and unreacted magnesia. At lower pressure such as 10 MPa and 50 MPa, the major phases in the outer shell were spinel, the MAO and unreacted magnesia and aluminum, while at high pressure 100 MPa to 250 MPa, the major phases in the outer shell were α-alumina, MAO and unreacted aluminum.

Increasing the briquetting pressure increased the contact area between MgO and Al and the thermal conductivity of the briquette, leading to an increased reaction rate. At the same time, increasing the briquetting pressure made the transfer of liquid aluminum from the central core to outer shell slower and the escape of magnesium vapour more difficult. The apparent effects of briquetting pressure on the reduction ratio of magnesia and the phase constitutions of the briquette residues were the combined result of above factors.

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