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Mechanism of Carbothermic Reduction of Magnesia and Reversion Reaction

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Abstract

In this study, the mechanism of the carbothermic reduction process to extract magnesium from magnesia and the reversion reaction in vacuum were investigated. The carbon monoxide (CO) content of the gas, phases of the condensing product, surface morphology of the reduction slag and phase of the distillation product were measured by means of gas chromatography (GC), XRD, and SEM. The experimental results indicated that Mg was generated by magnesia and carbon at 1623K and 30~100Pa in the carbothermic reduction process.The main gas in carbothermic reduction process is carbon monoxide, no carbon dioxide occurred at any reaction time, the reduction reaction is $MgO_{(s)}+C_{(s)}=Mg_{(g)}+CO_{(g)}$. The gas-phase reversion will commence as soon as the saturated gas mixture is cooled. The reversion reactions are favored below 1373K.The distillation product by vacuum distillation process produced high purity metal magnesium product, it can be deduced in reversion reaction which occured at low temperature and 30~100Pa during carbothermic reduction. The reversion reaction was calculated, which gave the peak value γ less than 9%.

Introduction

Magnesium is the eighth most abundant element in the Earth's crust (approximately 2.5% by weight)and does not occur uncombined[1]. It is also the lightest of all metals used for structural alloys[2]. Magnesium alloys have attracted increasing interest for mass reduction in aerospace, automobile industry and transportation[3].The requirement have triggered renewed interest in magnesium[4].Now, the pigeon process is the main method of thermal reduction of magnesium metal production, However, since the low reactivity of ferrosilicon alloy, the high temperature and long reaction time were needed[5].

Carbothermic reduction is an alternative to both silicothermic and electrolytic processes for the production of magnesium[6-7]. But the reversion reaction between Mg vapor and CO are major technical challenges. In order to avoid the reversion reaction, Hori points that thermal control of the product gases is important throughout the process from the reaction chamber to the product collection point via the nozzle[8-9]. Now Tassios's invention involves the manner of heated nozzle. The invention heat is supplied to the nozzle over-and-above any heat that is supplied to the nozzle by gas flow[10]. But all of the invention of reversion reaction between Mg vapor and CO were only considered as apparatus and method, the mechanism of reaction was not studied.

Recently our research group[11-12] focused on the mechanism of the reduction process and reversion reaction. The effects of carbothermic reduction process, reversion reaction ratio, and condensing product of vacuum distillation were discussed. In order to investigate the mechanism of the

carbothermic reduction process in vacuum, GC ,XRD and SEM techniques are also proposed.

Experimental

Raw material

Carbothermic reduction process: analytical grade of magnesia, carbon and CaF_2 were used as the raw materials in experiments.

Vacuum distillation process: condensing product of carbothermic reduction.

Schematic diagram of vacuum furnace

Experiments were carried out in a self-made vacuum furnace shown in Fig.1.

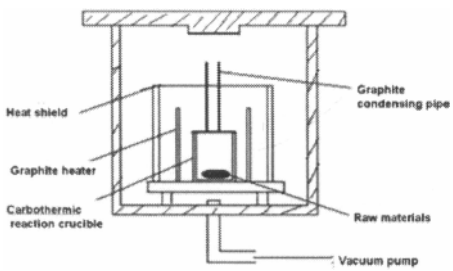


Fig.1 Schematic diagram of vacuum furnace:

Experimental procedure

Carbothermic reduction process: magnesia and carbon with a certain molar ratio (MgO/C=1/2) were mixed, and cast into pellets of Φ30mm×10mm under 2-10MPa as shown in the Fig. 2. The heating rate of system temperature was about 15K•min^{-1}. In the magnesia carbothermic reduction process, the prepared pellets were heated from room temperature to 1073K and held at this temperature for 20 minutes to remove the adsorbed gases and water. Then, the temperature was raised to 1473K-1773K. After the reaction time(2h to 5h), the reaction product was cooled to room temperature and took out. The reduction reaction in this process was $MgO_{(s)}+C_{(s)}=Mg_{(g)}+CO_{(g)}$, and the reversion reaction in this process was $Mg_{(g)}+CO_{(g)}=MgO_{(s)}+C_{(s)}$.

Vacuum distillation process: used the condensing product of carbothermic reduction as distillation materials directly as shown in the Fig.3, the heating rate of system temperature was about 15K•min^{-1}. In the process, the condensing product was heated from room temperature to 1373K. After the distillation time(1h or 2h), the distillation product was cooled to room temperature and took out. The reaction take place during distillation process was $Mg_{(l)}=Mg_{(g)}$.

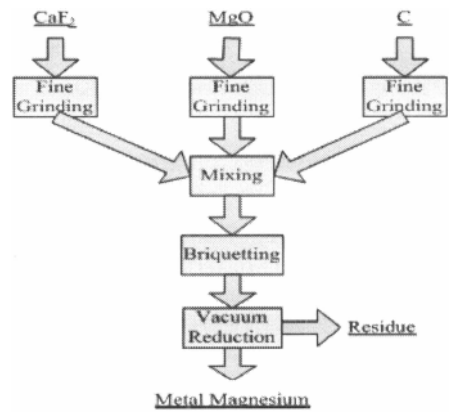


Fig. 2 Reduction experimental flow chart

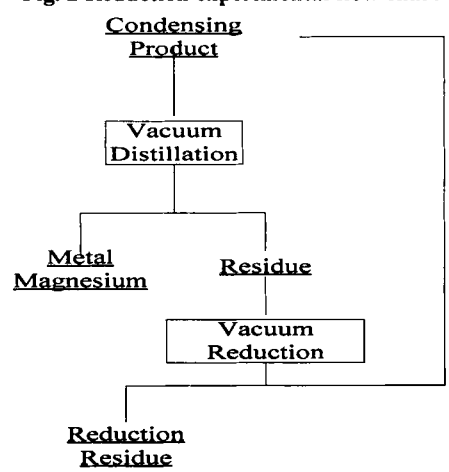


Fig. 3 Distillation experimental flow chart

Analysis methods

The crystalline phase of the products was identified by X-ray diffraction (XRD) instrument (D/max-3B) using Cu K。 radiation with a scanning rate of 2 (°)/min which was made by Rigaku Corporation of Japan. Surface morphology of the condensing product was characterized by scanning electron microscopy (XL30ESEM-TMP, Phillips, Holland). The content of carbon monoxide was determined with gas chromatography (6890N, Agilent Technologies, Taiwan).

Results and Discussion

3.1Analysis of magnesia carbothermic reduction process

The reactions of MgO and Carbon could occur at about 1625K and 10~100Pa[13], meanwhile, CO was generated continuously. Gas in the magnesia carbothermic reduction process was collected using the air-pocket at 60 minutes intervals, and the gas volume measured by drainage. The content of carbon monoxide was determined by GC. The volume of carbon monoxide per hour and total volume of carbon monoxide was calculated, and the average production rate of carbon monoxide per 60min determined.

Tab.1 Gas chromatography analysis of carbothemic reduction

Gas Compositions / Reaction Temperature	CO Content/%	CO_2 Content/%
1723K	39.59	0.00
1723K (after 1h)	27.91	0.00
1723K (after 2h)	58.21	0.00
1723K (after 3h)	61.11	0.00
1723K (after 4h)	54.29	0.00

Tab.1 shows the relationship between magnesia carbothermic reduction time at 1723K, the content of total volume of carbon dioxide and total volume of carbon monoxide. As shown in Tab.1, it can be seen that the main gas in carbothermic reduction process was carbon monoxide, no carbon dioxide occurred at any reaction time. Accordingly, the thermodynamic analysis of carbothermic process was assumed to generate gas approximation for 100%CO.The main reduction was $MgO_{(s)}+C_{(s)}=Mg_{(g)}+CO_{(g)}$.(1) The indirect reduction $MgO_{(s)}+CO_{(g)}=Mg_{(g)}+CO_{2(g)}$ (2) did not occur during the process.

Though the thermogravimetric reduction experiment, the mass loss of the sample was monitored as a function of time. The reduction ratio(α) at given instance was defined as $\alpha=\frac{M_0-M_1}{M_0}\times100\%$ (3)

where M_0 represents the initial mass of magnesium in the sample, and M_1 is the residual in the sample.

Fig.4 shows the relationships between the typical mass-loss percentage and temperature curve of reduction of magnesia by carbon. There was no massive loss detected when the temperature was below 1373K,indicating no reaction happens. When the temperature was higher than 1373K,the mass loss was less than 20% of the total mass, however, the temperature was above 1623K,the sample weight changed sharply with the increase of temperature. So the initial reduction temperature was 1623K, it was accorded with the theoretical calculation.

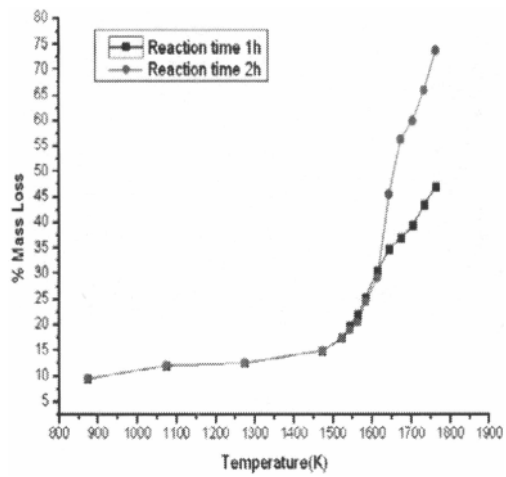
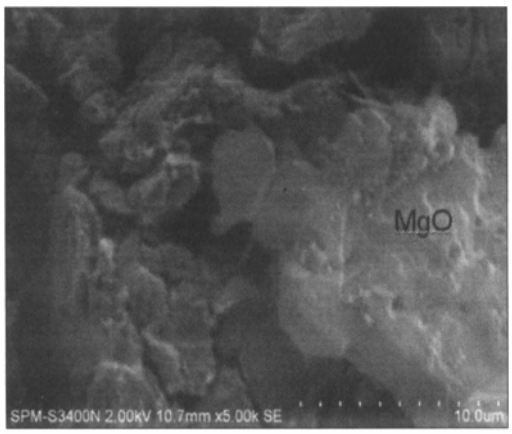
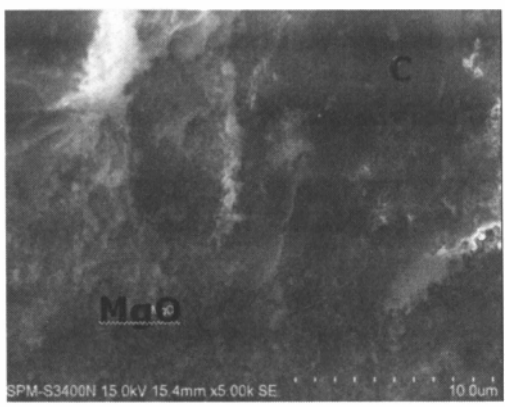


Fig. 4 Relationships of the Reduction temperature and α

Fig.5 shows the SEM micrographs of pellets of magnesia and carbon before and after experiments. In SEM micrographs, the white cluster structured particles were MgO, the black granuiar-structure particles were carbon. From the micrograph(Fig.5(a)), it can be seen that the particle size of MgO was big and the mixing condition between magnesia and carbon particles was good before experiment. Then it was found that the particle size of carbon decrease, and few MgO detected(Fig.5(b)). All these factors result in the decrease of the contacting area between magnesia and carbon particles.



(a)



(b)

Fig.5 The SEM micrographs of raw materials and reduction product samples: (a)the pellet of magnesia and carbon; (b)the residue obtained after carbothermic reduction at 1723K for 2h.

3.2 Analysis of reversion reaction

A number of possible reversion reactions can take place during cooling of an Mg/CO/inert gas mixture:

gas phase reversion reaction:

$Mg_{(g)}+CO_{(g)}=MgO_{(s)}+C_{(s)}$ (4)

liquid-phase reversion reaction:

$Mg_{(l)}+CO_{(g)}=MgO_{(s)}+C_{(s)}$ (5)

solid-phase reversion reaction:

$Mg_{(s)}+CO_{(g)}=MgO_{(s)}+C_{(s)}$ (6)

The Gibbs free energy of reaction (4),(5),(6) at different temperatures and pressures were evaluated and the results reported in Fig.6.Thermodynamically, these reversion reactions were exothermic reaction, the gas-phase reversion will commence as soon as a saturated gas mixture was cooled. The magnesium condensation and liquid-phase reversion reaction were favored below 1373K, and magnesium solidification and liquid-phase reversion reactions were favored below 973K. It can be seen that these reversion reactions will be favored over the metal-forming reactions during cooling, meaning that the relative kinetics of each reaction will be critical to any process designed to produce metal. Fig.7 shows the XRD patterns of the condensing product in carbothermic reduction, it can be seen that metal magnesium was obtained. Meanwhile, magnesia was also found.

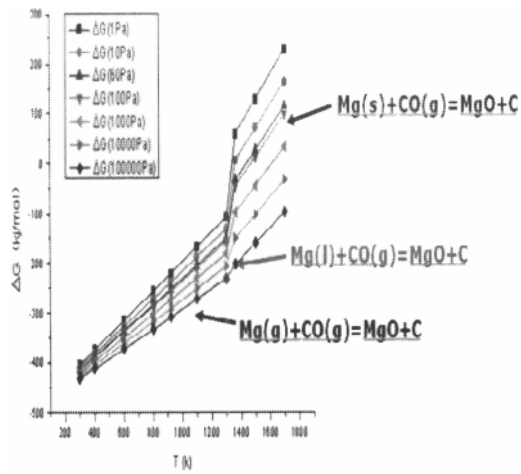


Fig. 6 Free energy changes related to the temperature of reaction(4),(5),(6) under different pressure

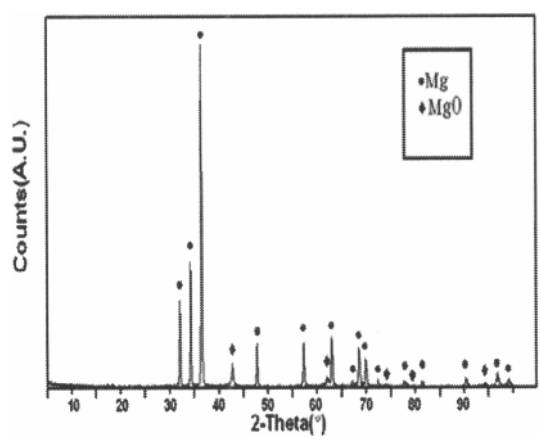


Fig.7 XRD patterns of the condensing product in carbothermic reduction

3.3 Analysis of vacuum distillation

After 1h(or 2h) of the vacuum distillation process ($Mg_{(l)}=Mg_{(g)}$), magnesia and carbon were loaded into

the reaction crucible; metal magnesium was produced in the condensing towers. As can be seen from the XRD patterns of vacuum distillation product shown in Fig.8, it demonstrates that all peaks were sharp and well-defined, which indicated the high purity of the metal magnesium. Comparing the results of condensing product before and after vacuum distillation, it can be deduced that reversion reaction occured at low temperature and 30~100Pa during carbothermic reduction.

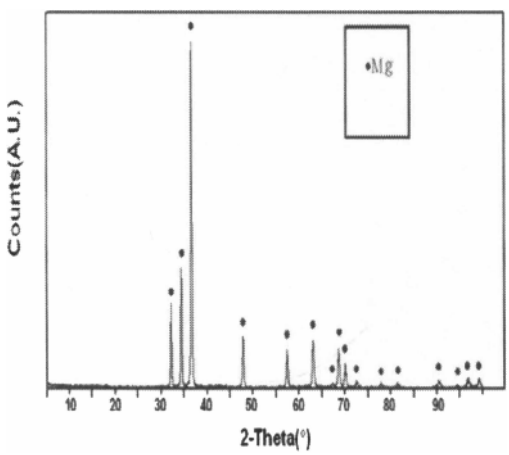


Fig.8 XRD patterns of distillation product

The reversion reaction ratio(γ) is defined as

$$\gamma = \frac{W_1}{W_0} \times 100\% \qquad (7)$$

where W_0 represents the total mass of magnesium and magnesia in the condensing product, and W_1 is the mass of magnesia in distillation residual.

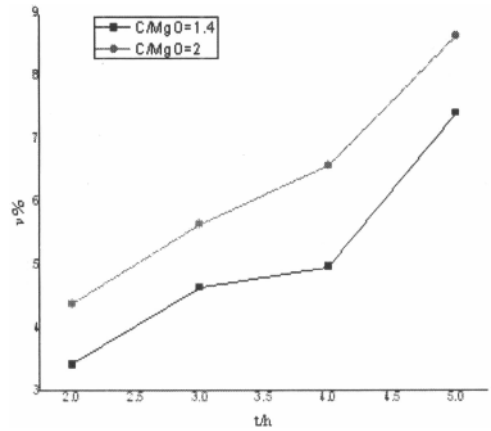


Fig.9 Relationships between reversion ratio and reaction time in different molar ratio

As shown in Fig.9, it was clear that the reversion reaction ratio changed slowly with the incremental molar ratio, the reversion reaction ratio increased with increasing reaction time. However, the peak value was less than 9%, it can be deduced that most magnesium vapor transforms into metal magnesium, the condensing condition of the vacuum equipment was appropriate for the carbothermic reduction.

Conclusions

1) In the carbothermic reduction process, Mg was generated by magnesia and carbon at 1623K and 30~100Pa. The main gas in carbothermic reduction process was carbon monoxide, no carbon dioxide occurred at any reaction time, the reduction reaction was $MgO_{(s)}+C_{(s)}=Mg_{(g)}+CO_{(g)}$.

2)Thermodynamically, the three reversion reactions are exothermic reaction, the gas-phase reversion will commence as soon as a saturated gas mixture was cooled. The reversion reactions were favored below 1373K.

3) The distillation product by vacuum distillation process produced a high purity metal magnesium product. Through the calculation of reversion reaction, the peak value of γ was less than 9%.

Acknowledgments

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