

Study on the Thermodynamic and Experimental Carbothermic Reduction of Garnierite

Tao Qu * Yang Tian Bin Yang Da-chun Liu
Bao-qiang Xu Yong-nian Dai

(1 National Engineering Laboratory for Vacuum Metallurgy, Kunming 650093, China;

2 Key Laboratory of Nonferrous Metals Vacuum Metallurgy of Yunnan Province, Kunming 650093, China;

3 Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology,
Kunming 650093, China

4 State Key Laboratory Breeding Base of Complex Nonferrous Metal Resources Clear Utilization in
Yunnan Province, Kunming 650093, China)

*Correspondence: Tel: +8613518715200; E-mail: qutao_82@126.com

Keywords: garnierite; carbothermic reduction; magnesium; vacuum metallurgy; thermodynamics

Abstract: The overall utilization of magnesium and other metals should be systematically considered during the exploration of deficient garnierite. In this paper the thermodynamic analysis of the carbothermic reduction process for extracting metal magnesium from garnierite in vacuum was carried out to investigate its feasibility. The calculation results indicate that it is feasible technically that the carbothermic reduction process for extracting metal magnesium from garnierite in vacuum. Under the temperature of 1500°C and vacuum degree is less than 300Pa, metal magnesium was obtained. The Nickel content in residue is more than twice as garnierite ore.

1. Introduction

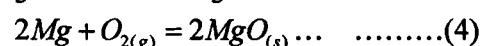
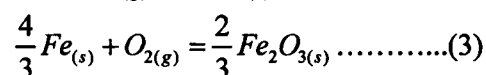
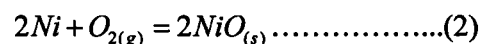
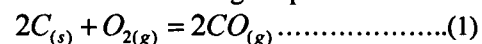
Garnierite is not a single mineral but a mixture of the Ni-Mg-hydrosilicates serpentine, talc, sepiolite, chlorite and smectite. Garnierite is a hydrous nickel silicate, with the serpentine group of minerals, mostly a mixture of various Ni- and Ni-bearing magnesium layer silicates[1-2]. It is an alteration of olivine, serpentine rocks, and can be associated with olivine, serpentine, chromite and talc. Garnierite is mined from laterite deposits, formed by weathering and secondary mineralization of igneous rocks. The nickel is

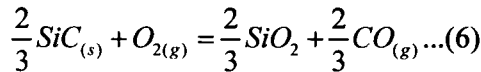
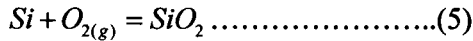
contained in the blue-green bands of the ore. The specific gravity of this mineral ranges from 2.3 to 2.8.

The Pyrometallurgical techniques are suited to treat garnierite, with processes typically involving drying, calcining, reduction and electric furnace smelting to produce a ferronickel[3-7]. The hydrometallurgical process is mainly used ammonia-ammonium carbonate leaching [8] and hydrochloric acid leaching [9]. All of these methods have a disadvantages is that the magnesium is not utilized well.

2. Thermodynamic Analysis

According to the test purposes, the main consideration in the nickel laterite NiO, Fe₂O₃, MgO and SiO₂ are that reduction of four major oxides and the possible reactions. First, consider the following a few basic oxidation reaction (phase state does not indicate that there is phase transition), according to Gass's law to determine possible reaction and starting temperature.





In this paper, the Gibbs free energy of material function was studied, the Gibbs free energy changes of the reaction temperature at various points were calculated by equation (2-1), (2-2), (2-3), (2-4) and thermodynamic data of inorganic reference manual[10], the calculation process is omitted.

$$\Delta\Phi_T = \sum(n_i\Delta\Phi_{i,T})_{product} - \sum(n_i\Delta\Phi_{i,T})_{reactant} \quad (2-1)$$

$$\Delta H_{298}^\theta = \sum V_i \Delta H_{298}^\theta(\text{product}) - \sum V_i \Delta H_{298}^\theta(\text{reactant}) \quad (2-2)$$

$$\Delta G_T^\theta = \Delta H_{298}^\theta - T\Delta\Phi_T \quad (2-3)$$

$$\Delta G_T = \Delta G_T^\theta + RT \ln J^\theta(T) \quad (2-4)$$

Fig.1 shows the relationship between the Gibbs free energy changes of the main oxidate and temperature. The reaction and conditions of the lines 1-12 were shown below Fig.1, $P_{(O_2)} = P^\theta = 10^5 Pa$. According to Gass's law, the Gibbs free energy of the reaction between material and 1mol O_2 is becoming negative, the substance out of the more difficult to be reduced under a certain temperature, instead the substance can be reduced which ΔG_T larger than it. The lowest initial reaction temperature point is the intersection point of the two lines.

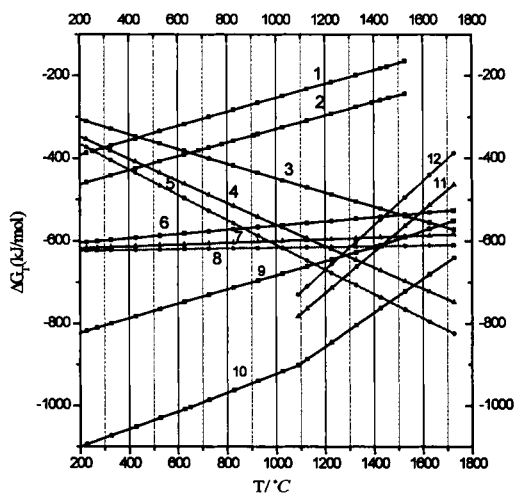
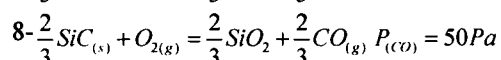
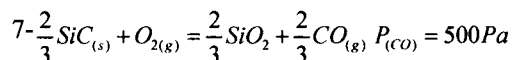
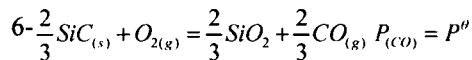
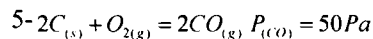
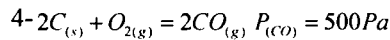
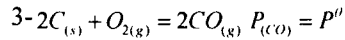
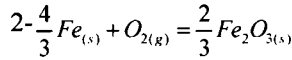
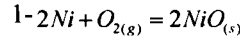
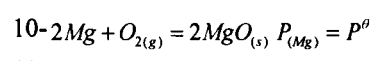


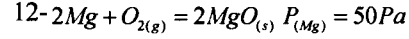
Fig.1 The relationship between the Gibbs free energy changes of the main oxidate and temperature



9-



11-



It can be seen from Fig.1 that NiO and Fe_2O_3 are poor stability, it can be reduced by C or Si at low temperatures Under atmospheric pressure above 450 °C the NiO can be reduced by C; Fe_2O_3 at 650 °C was reduced by C too, Lower initial reaction temperature is in vacuum; SiO_2 , and MgO are stable, it can be reduced under higher temperature. Consider that the total pressure is 30-500Pa in furnace, the reduction temperature of SiO_2 and MgO decreased significantly.

Fig.2 shows that Fig.1 was magnified and remove the other reaction (2), (3), (5), (6) in order to facilitate observation, it can be seen that A: $P_{(CO)} = P_{(Mg)} = 50Pa$, MgO can be reduced by C under 1473K ; C: $P_{(CO)} = P_{(Mg)} = 500Pa$, MgO can be reduced by C under 1623K; At atmospheric pressure the reaction temperature is 1832K. However, we can see reaction (1) and (4) in the region will intersect within ABCD, that means between 1473K and 1623K, the carbothermic reduction magnesia is easily occurred.

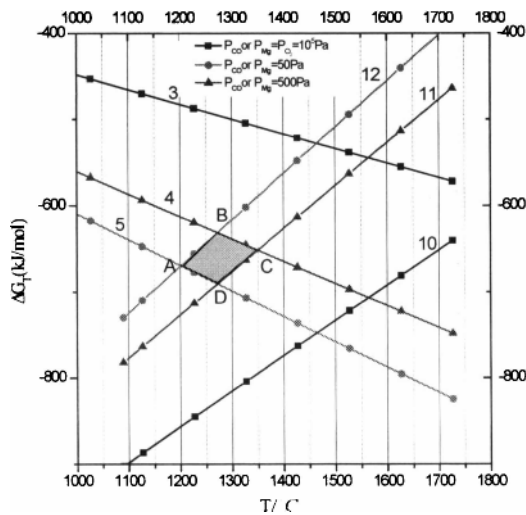


Fig.2 The relationship between the Gibbs free energy changes of MgO, CO and temperature

The above analysis shows that the carbothermic reduction magnesia is easily occurred under vacuum conditions. But the reverse reaction $Mg_{(g)} + CO_{(g)} = MgO_{(s)} + C_{(s)}$ [11] is also occurred.

3. Experimental

3.1 Materials

The materials used in this study were garnierite and coal with CaF_2 ($CaF_2 \geq 98\%$) as catalyst. The chemical composition of garnierite ores and coal were given in Table.1 and Table.2. And the XRD pattern of garnierite is shown in fig.3.

Tab.1 Chemical composition of garnierite

composition	Ni	MgO	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃
wt%	1.18	27.74	11.10	36.91	2.73

Tab.2 composition of coal

composition	M _{ad}	V _{daf}	A _d	FC _d
wt%	0.78	16.43	19.21	63.58

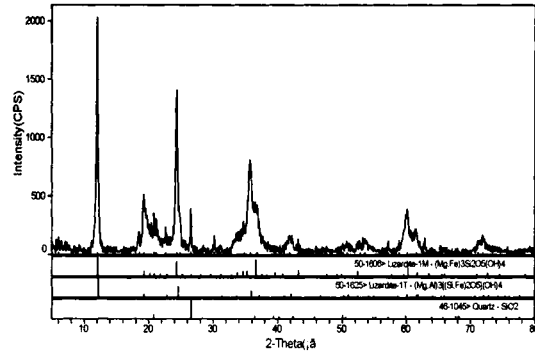
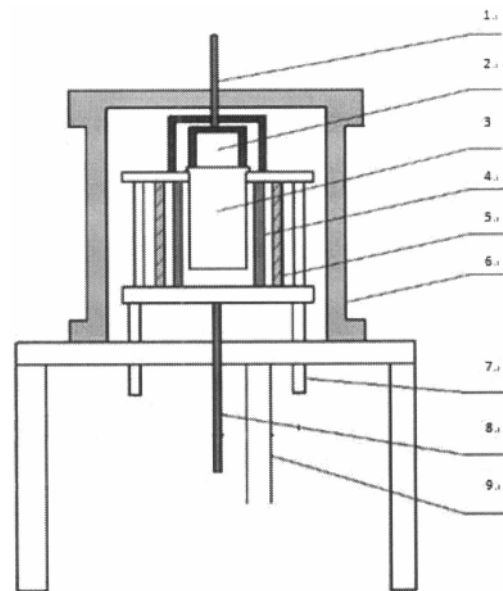


Fig.3 the XRD pattern of garnierite

3.2 Experimental device

The experimental device for vacuum thermal reduction is shown in Fig.4, which is composed of reactor, temperature control system, vacuum system and condenser system.



1. thermocouple; 2. condenser; 3. couple; 4. heating unit; 5. thermal insulating layer; 6. furnace; 7. electrode; 8. thermocouple; 9. exhaust pipe

Fig.4 Experimental device

3.3 Experimental method

In the vacuum and high temperature conditions, coal can reduce magnesium silicate and get magnesium vapor, and condense it for getting magnesium metal. The technological flow sheet is shown in Fig.5.

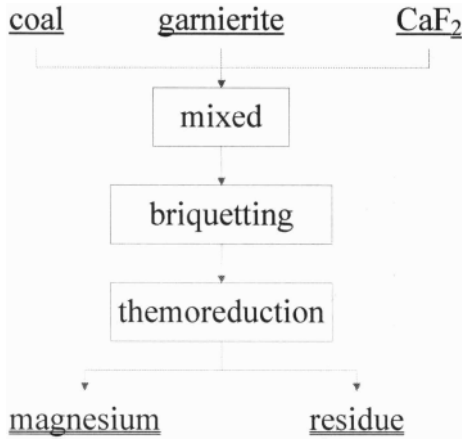


Fig. 5 Technical flow sheet of extracted magnesium from the garnierite

4 Results and Discussion

4.1 The magnesium extracted from the garnierite

On the condition of reduction temperature 1500°C, vacuum degree is less than 300Pa, briquetting pressure 8 MPa, reduction time 90min, and with 5% CaF₂, we can get some magnesium. The photo and XRD pattern of magnesium is shown in the Fig.6, and the EDX is shown in Fig.7.

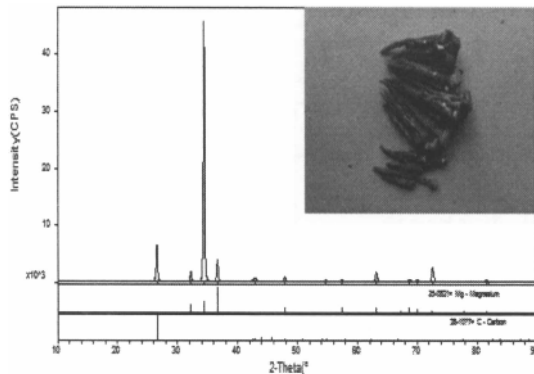


Fig.6 The photo and XRD pattern of magnesium

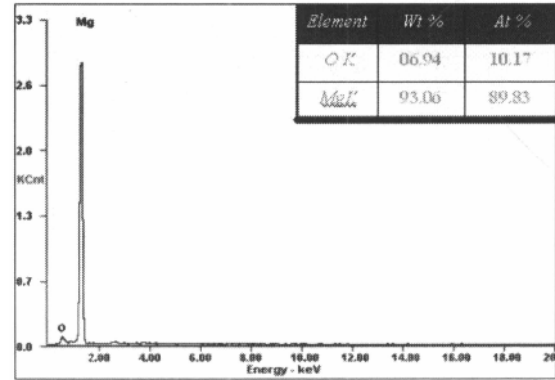
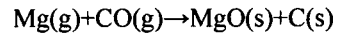


Fig.7 The EDX of magnesium

From the XRD and EDX analysis, we can know that there has some oxygen and carbon in the magnesium. We believe the oxygen and carbon get from the reverse reaction of reduction, the reaction formula is as following:



4.2 The XRD analysis of residue

On the condition of reduction temperature 1500°C, vacuum degree is less than 300Pa, briquetting pressure 8 MPa, reduction time 90min, and with 5% CaF₂, the XRD pattern of residue is shown in the fig.8.

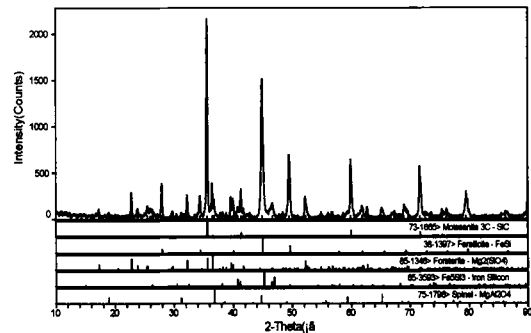


Fig.8 The XRD pattern of residue

It can be seen that there mainly are the phases of SiC and FeSi, and also contained some Mg₂SiO₄, MgAl₂O₄. It's shown that the MgO and SiO₂ still no reaction completely, and Si generated the SiC(main), FeSi and Fe₅Si₃, and it's not found the Iron and silicon elemental. Nickel does not be detected, mainly because of its content is low.

4.3 Effects of reduction time on reduction rate of magnesium

On the condition of reduction temperature 1500°C, vacuum degree is less than 300Pa,

briquetting pressure 8 MPa, and with 5% CaF₂, the reduction rate of magnesium by coal at varying time conditions are shown in Fig.9. In these experiments, the reduction time is that the temperature of reactor keeps the 1500°C after it is reach. As is shown from the chart, with the extension of reaction time, reduction rate of magnesium is increased. But when the reduction time is reached 90min, the curve has become flat, the reduction rate of magnesium with the increase in reaction time is not obvious.

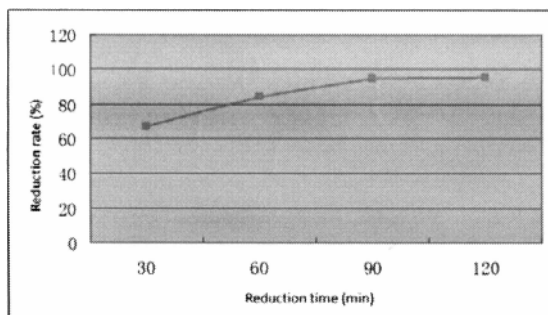


Fig.9 Relationship between reduction rate and time

4.4 Effects of reduction time on nickel content of residue

On the condition of reduction temperature 1500°C, vacuum degree is less than 300Pa, briquetting pressure 8 MPa, and with 5% CaF₂, the nickel content of residue at varying time conditions are shown in Fig.10. As is shown from the chart, with the extension of reaction time, the nickel content is increased. When the reduction time is reached 90min, the Nickel content is more than twice as garnierite ore.

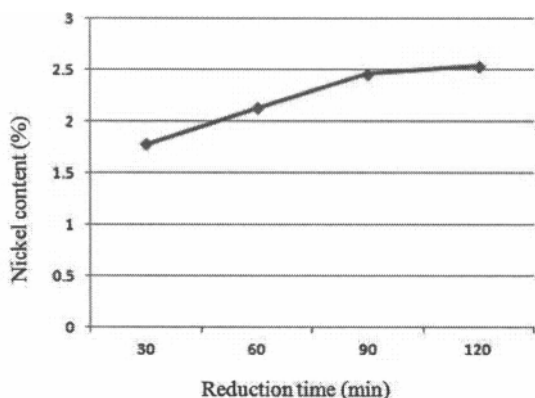


Fig.10 Relationship between nickel content and reduction time

5. Conclusion

In this paper, the coal was used to reduce the garnierite to prepare metal magnesium in vacuum. We can get the following conclusion:

1. The thermodynamic calculation results indicated the $P_{(CO)} = P_{(Mg)} = 50\text{Pa}$, that reduction temperature is down to 1473K from 1832K at atmospheric pressure.

2. This method can prepare the magnesium from garnierite, but has small amount oxygen and carbon, it should be got from the reverse reaction of reduction.

3. SiC and FeSi were obtained in residues by carbothermic reduction garnierite under a temperature of 1500°C, and it's not found the Iron and silicon elemental.

4. The reduction rate of magnesia is enhance with the extensive reduction time.

5. The nickel content is enhance with the extensive reduction time, when the reduction time is 90min, the Nickel content in residue is more than twice as garnierite ore

Acknowledgements

This work was financially supported by Science Research Foundation of Education Department of Yunnan Province, China (No. 2010C257)

Reference

- [1] Andrew B, Jeffrey H, Angus J M, et al, Development of a model for serpentine quantification in nickel laterite minerals by infrared spectroscopy, Minerals Engineering, 2010, vol23: 407-412;
- [2] Sun Chuanyao, Yin Wanzhong, flotation principle of silicate minerals, Beijing, China: Science Press, 2001;
- [3] Legendijk H, Schouken S. A. F. S, Smith P, et al. The production of ferronickel from nickel-containing laterite, South African Patent, EPI9940306256, 2004.05.19;
- [4] Nayak J. C, Production of Ferro-nickel from Sukinda Laterites in Rotary Kiln-electric

Furnace, *Transaction of Indian Metallurgy*, 1985, 38(3): 241-247

[5] Watanabe T, Ono S, Arai H, et al, Direct Reduction of Garnierite Ore for Production of Ferronickel with a Rotary Kiln at Nippon Yakin Co. Ltd. Oheyama Works, International Seminar on Laterites, MMIJ, Tokyo, 1985: 103-115

[6] Tanaka K, Sakamoto K, Sato K, Production of ferronickel by blast furnace at Nippon Mining's Sagamosaki smelter and refinery, International Seminar on Laterites, MMIJ, Tokyo, 1985: 127-137;

[7] Ishii K, Development of Ferro-Nickel Smelting from Laterites in Japan, International Seminar on Laterites, MMIJ, Tokyo(1985): 13-24;

[8] Power L. F, Geiger G. H, The application of the reduction roast-ammoniacal ammonium carbonate leach to nickel laterites, *Minerals Science*, 1997, 9(1): 32-50

[9] Dutrizac, J.E. Chen, T.T. White, C.W. Fundamentals of serpentine leaching in hydrochloric acid media [J]. *TMS Annu Meet.* 2000:41~51;

[10] Dai Yong-nian, Yang Bin Vacuum metallurgy of nonferrous materials. Beijing, China: Metallurgical industry press. 2003

[11] Rong-ti, PanWei, Masamichi Sano, Li Jian-qiang, *Thermochimica Acta*, 398 (2003) : 265 - 267