

## High temperature dephosphorization behavior of monazite concentrate with charred coal

XING Peng-fei(邢鹏飞), ZHUANG Yan-xin(庄艳歆), TU Gan-feng(涂赣峰), GUO Jing(郭菁)

School of Materials and Metallurgy, Northeastern University, Shenyang 110004, China

Received 17 December 2009; accepted 27 April 2010

**Abstract:** Dephosphorization behavior of monazite concentrate with charred coal at high temperature was investigated. It is found that the roast temperature is the main factor for the dephosphorization of the monazite. The high dephosphorization efficiency can be reached at the temperatures ranging from 1 200 to 1 400 °C. When the monazite pellets, made by pressing mixture of the monazite, charred coal and water into mould, were roasted at 1 400 °C for 2 h, 98% of phosphorus was removed from the monazite pellets. The roast time has little effect on the dephosphorization efficiency. Meanwhile, the particle size of the charred coal also has great influence on the dephosphorization efficiency of the monazite, and it is better to control particle size around 150 μm, while Fe and Fe<sub>2</sub>O<sub>3</sub> have neglectable effect on the dephosphorization of the monazite.

**Key words:** dephosphorization; monazite concentrate; charred coal; high temperature

### 1 Introduction

Rare earth (RE) ferrosilicon alloys have been widely used as intermediate alloys in iron and steel, machinery, automotive and military industry[1–2]. The rare earth intermediate alloys are mainly fabricated by silicon thermal reduction method (SRM) and carbon thermal reduction method (CRM)[3]. The CRM can be regarded as a short, low-cost and environment-friendly process, which has great potential industrial application[4]. Nevertheless, up to now, the CRM is only successful in preparing RE-alloys from the bastnaesite ore[5], and cannot be applied to the Baotou ore due to its high phosphorus content ( $w(\text{P}_2\text{O}_5)$  of 4%–10%). Baotou ore is a mixed ore, which consists of 60% monazite and 40% bastnaesite. The main component of the monazite is rare earth phosphate ( $\text{REPO}_4$ ). In the metallurgy process, the reaction between the phosphorus and RE will take place, and results in the formation of various phosphides, which causes pulverization of the RE-alloys[6–7]. Therefore, it is very important to remove the phosphorus from the ore and to decrease the amount of the phosphorus entering into the alloys[8]. ZHAO et al[9] studied the carbon-thermal reduction process of rare

earth concentrate with high-content phosphorus. WU et al[10] investigated the thermal-decomposition mechanisms of the mixed rare earth concentrate containing monazite. ZHANG et al[11] explored the dephosphorization techniques of high-content phosphorus concentrate in electric arc furnace. TU et al[12] reported the dephosphorization kinetics of lanthanum phosphate using carbon. However, to our knowledge, there is no report about the dephosphorization behavior of the monazite with charred coal.

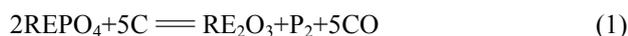
Due to its high thermal stability, the rare earth phosphate is very difficult to decompose even at a high temperature, and hereby it is infeasible to dephosphorize through high temperature roasting. In chemical industry, it has been well known that the phosphorus can be fabricated through reduction of calcium phosphate using carbon followed by evaporation and condensation of the phosphorus ( $\text{Ca}_3(\text{PO}_4)_2 + 5\text{C} = 3\text{CaO} + \text{P}_2 + 5\text{CO}$ )[13–14], similar mechanism can be used to remove the phosphorus from the monazite. We have reported the dephosphorization behavior of the monazite using coking coal as a reductant[15]. In this work, the dephosphorization of the monazite using charred coal is also investigated by the same technique under different conditions. The effects of particle size of the charred

coal, roast temperature, roast time, Fe and Fe<sub>2</sub>O<sub>3</sub> on the dephosphorization behavior were investigated. The results provide technical support for realization of preparing RE alloy from the Boutou ore using the CRM in the future.

## 2 Experimental

The monazite concentrate powder with the particle size of 75 μm was from Hunan Taojiang smelter, China. It consisted of 62.20% RE oxide (REO) and 9.74% P<sub>2</sub>O<sub>5</sub>. Among the REO, the main materials were CeO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, Pr<sub>6</sub>O<sub>11</sub> and Nd<sub>2</sub>O<sub>3</sub>. The charred coal, used as a reductant, consisted of 76.3% carbon, 17.2% volatile and 6.5% ash. The particle sizes of the charred coal were 75, 109, 150, 250, and 380 μm, respectively. A residual oil, which consisted of 50% carbon and 50% volatile, was added as an adhesive to improve the compressive strength of pellets. The purities of Fe and Fe<sub>2</sub>O<sub>3</sub> were larger than 99%, and the particle size was 75 μm.

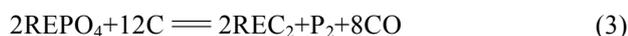
In the process of CRM, the monazite is firstly reduced to RE<sub>2</sub>O<sub>3</sub> by carbon in the submerged arc furnace, and the reaction can be expressed as



Then, the RE<sub>2</sub>O<sub>3</sub> further reacts with carbon to form REC<sub>2</sub> according to the following reaction:



The total reaction between REPO<sub>4</sub> and C is



The theoretical mass ratio of materials used in the dephosphorization process of the monazite can be calculated from reaction(3). Considering the burning loss of carbon, the amount of carbon was actually 1.2 times the theoretical amount. The mass ratio of the materials of monazite, charred coal, water and residue oil was 100:43:10:5 (The average molecular mass of RE used in the calculation is 140). The pellets were fabricated by pressing the mixture of above materials at the pressure of 18 MPa. Then the pellets were heated up to 500 °C for baking.

To remove the phosphorus, the pellets were roasted at 1 100, 1 200, 1 250, 1 300, 1 350, and 1 400 °C, respectively. The pellets were placed into a graphite crucible, covered with charred coal powder, and then loaded into a furnace that was preheated to the desired temperatures. After being kept at the temperature for a given time, the pellets were taken out from the furnace and cooled down to room temperature for further analysis. The content of phosphorus in the pellets was determined by quantitative chemical analysis method. The structure of the samples was characterized by X-ray diffractometer (XRD) using Cu K<sub>α</sub> radiation

(Rigaku-D/max).

## 3 Results and discussion

### 3.1 High temperature dephosphorization of monazite

After being roasted at high temperature, the baked pellets became light with unchanged volume. When the roasting temperature was higher than 1 200 °C, a large number of white smokes generated after pellets were loaded into furnace. Afterwards, a lot of brown solid powders, which are red phosphorus as determined by XRD, have been found at the end of the furnace, meaning that the phosphorus have been significantly removed from the pellets at 1 200 °C. Fig.1 illustrates the dephosphorization efficiency of the monazite as a function of the roasting temperature and time, where the particle size of the charred coal is 150 μm. The roasting temperature has great impact on the dephosphorization efficiency. The dephosphorization rate reaches 18.2% at 1 100 °C for 1 h, suggesting that the dephosphorization process starts at 1 100 °C even though the dephosphorization rate is relative low. The dephosphorization ratio increases with the increase of roasting temperature. Especially, at the temperature between 1 200 °C to 1 400 °C, the dephosphorization rate increases rapidly with the increase of temperature, meaning that the temperature has stronger effect on the reaction rate. The dephosphorization rate reaches 98% at 1 400 °C for 2 h, indicating that most of the phosphorus in the pellets has been removed and further higher roasting temperature will be unnecessary. The dephosphorization behavior is also enhanced by increasing the roasting time. The longer roasting time is helpful for removing phosphorus in the system. However, with increasing the temperature, the time becomes less important. For example, at 1 400 °C, further longer roasting time than 2 h is not necessary since the most of phosphorus has been removed after 2 h. It can be concluded that the temperature is a main factor for the dephosphorization of the monazite.

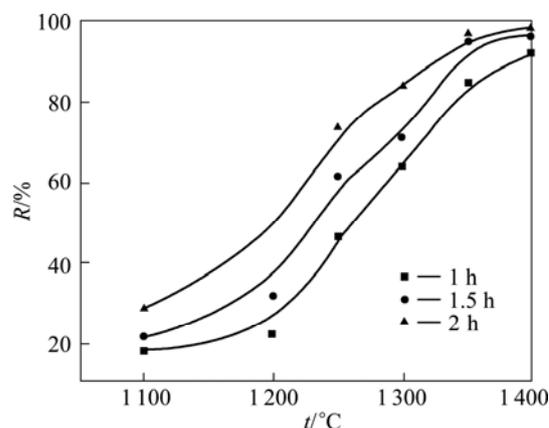
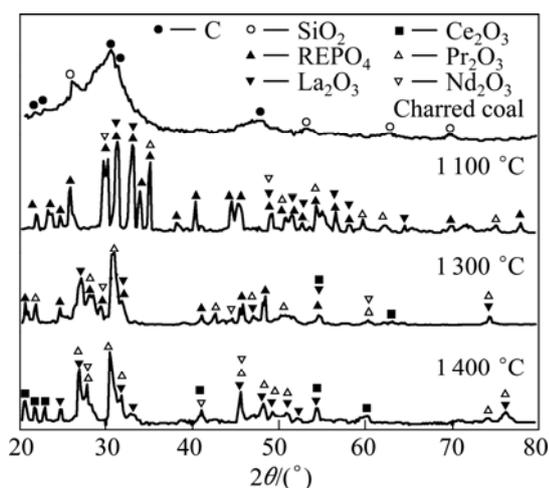


Fig.1 Relationship between dephosphorization rate *R* of monazite and roasting temperature *t* and time

Fig.2 shows the XRD patterns of the charred coal and pellets of the monazite roasted at various temperatures for 2 h. The main contents of the charred coal are carbon and small amount of SiO<sub>2</sub>. After being roasted at 1 100 °C for 2 h, the pellets consists of REPO<sub>4</sub> and a small amount of La<sub>2</sub>O<sub>3</sub>, Ce<sub>2</sub>O<sub>3</sub>, Pr<sub>2</sub>O<sub>3</sub> and Nd<sub>2</sub>O<sub>3</sub>, indicating that only small amount of REPO<sub>4</sub> is reduced to the REO, and the reaction rate is relative low. However, at 1 300 °C, the most of REPO<sub>4</sub> in the pellets was reduced to REO, indicating that the reaction rate increases with the increase of temperature. At 1 400 °C, only the peaks of La<sub>2</sub>O<sub>3</sub>, Ce<sub>2</sub>O<sub>3</sub>, Pr<sub>2</sub>O<sub>3</sub> and Nd<sub>2</sub>O<sub>3</sub> have been found on the XRD pattern, no REPO<sub>4</sub> has been found in the limitation of XRD detection, suggesting that the REPO<sub>4</sub> in the pellets has been reduced to REO, which is in agreement with the conclusions above. Therefore, the charred coal is very effective to remove phosphorus from the monazite in the temperature range of 1 200–1 400 °C.



**Fig.2** XRD patterns of charred coal and pellets of monazite after being roasted at various temperatures for 2 h

Table 1 gives the standard Gibbs free energy and theoretical initial reaction temperature of the reaction between REPO<sub>4</sub> with carbon, which are obtained from the thermodynamic calculation at the standard state. The

theoretical initial reaction temperature is 1 231 °C for the reduction reaction between LaPO<sub>4</sub> and C, 1 325 °C for the reaction between CePO<sub>4</sub> and C, 1 225 °C for the reaction between PrPO<sub>4</sub> and C, and 1 251 °C for the reaction between NdPO<sub>4</sub> and C, respectively. However, the partial pressure of P<sub>2</sub> and CO in the reaction system has effect on the initial reaction temperature. For example, in the reaction system, the CePO<sub>4</sub> reacts with C to form Ce<sub>2</sub>O<sub>3</sub>, the theoretical initial reaction temperature is 1 598 K (1 325 °C) as given in Table 1. However, when the pressure ratio of P<sub>2</sub> to CO is 5:1, Gibbs free energy for the reaction is

$$\begin{aligned} \Delta G_2 &= \Delta G_2^\ominus + RT \ln \frac{(p_{P_2} \times p_{CO}^5)}{(p^0)^6} \\ &= 1\,822\,806 - 1\,140.68T + 8.3147T \ln \left( \frac{1}{6} \times \left( \frac{5}{6} \right)^5 \right) \\ &= 1\,822\,806 - 1\,163.16T \end{aligned} \quad (4)$$

Assuming  $\Delta G_2=0$ , then the initial reaction temperature is 1 293 °C for the practical reaction system, meaning that the real initial reaction temperature is lower than the theoretical one. The real initial reaction temperatures at the condition of V(CO):V(P<sub>2</sub>)=5:1 for all the five reactions are also given in Table 1 for comparison.

In the practical production, under the conditions of temperature larger than 1 000 °C and larger amount of carbon existing, most of carbon will become CO. Meanwhile, the pressure of P<sub>2</sub> is very small in the reaction system, meaning that the volume ratio of CO to P<sub>2</sub> will be significantly larger than 5:1. On the other hand, there are other impurities in the system, which cause other reduction gas such as H<sub>2</sub>O and SiO presenting at high temperature. Considering all the practical condition, the dephosphorization reaction of the monazite will actually start at even lower temperature. This is the reason why the dephosphorization starts even at 1 100 °C as found in the work. The higher temperature will enhance the dephosphorization of the monazite according to Eq.4. The results above suggest that the charred coal is an effective agent for dephosphorization.

**Table 1** Standard Gibbs free energy  $\Delta G^\ominus$ , theoretical initial reaction temperature  $t_0$  and real initial reaction temperature  $t$  at condition of V(CO):V(P<sub>2</sub>)=5:1 for reaction of rare earth phosphate with carbon

Reaction equation	$\Delta G^\ominus / (\text{J} \cdot \text{mol}^{-1})$	$t_0 / ^\circ\text{C}$	$t / ^\circ\text{C}$
$2\text{LaPO}_4 + 5\text{C} = \text{La}_2\text{O}_3 + \text{P}_2 + 5\text{CO}$	$\Delta G_1^\ominus = 1863930 - 1239.7 T$	1 231	1 201
$2\text{CePO}_4 + 5\text{C} = \text{Ce}_2\text{O}_3 + \text{P}_2 + 5\text{CO}$	$\Delta G_2^\ominus = 1822806 - 1140.7 T$	1 325	1 293
$2\text{PrPO}_4 + 5\text{C} = \text{Pr}_2\text{O}_3 + \text{P}_2 + 5\text{CO}$	$\Delta G_3^\ominus = 1856790 - 1239.2 T$	1 225	1 198
$2\text{NdPO}_4 + 5\text{C} = \text{Nd}_2\text{O}_3 + \text{P}_2 + 5\text{CO}$	$\Delta G_4^\ominus = 1884160 - 1236.7 T$	1 251	1 196
$2\text{CePO}_4 + 5\text{C} = \text{CeO}_2 + \text{P}_2 + 4\text{CO}$	$\Delta G_5^\ominus = 1596640 - 971.0 T$	1 361	1 336

### 3.2 Effect of charred coal sizes on dephosphorization

Since the pellets made of the monazite and reductant powder were used in the process of the CRM, the contact area between the monazite and charred coal, i.e. the particle size of the reaction materials is very important for the reaction rate. Fig.3 shows the dephosphorization rate as a function of particle size of the charred coal, where the particle size of the monazite remains 75  $\mu\text{m}$ , and the pellets are roasted at 1 400  $^{\circ}\text{C}$  for 2 h. It can be seen that the dephosphorization rate increases with the decrease of the particles size of the charred coal. However, when the particle size is smaller than 150  $\mu\text{m}$ , the particle size of the charred coal has less important effect on the dephosphorization efficiency. Therefore, the optimized particle sizes of the charred coal should be about 150  $\mu\text{m}$ .

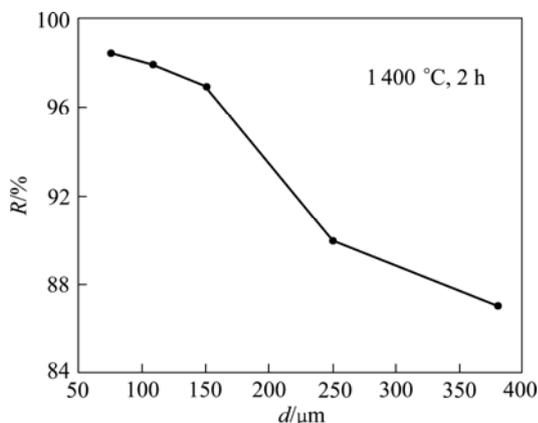


Fig.3 Influence of particle size  $d$  of charred coal on dephosphorization rate  $R$  of monazite

### 3.3 Effect of Fe and $\text{Fe}_2\text{O}_3$ on dephosphorization

It is well known that the electrodes of the submerged arc furnace are covered with a layer of iron. During the reaction, the iron will be continuously melted into the reaction system. In the production process, some of iron will be unavoidably introduced into the alloys. Meanwhile, there are a small amount of iron oxides in the Baotou ore. Therefore, it is necessary to know the effect of iron and iron oxide on the dephosphorization rate of the monazite.

Fig.4 shows the dephosphorization rate as a function of iron content, where the particle size of the monazite and the charred coal are 75 and 150  $\mu\text{m}$ , respectively. It can be found that the iron has little effect on the dephosphorization of the monazite at 1 300, 1 400 and 1 500  $^{\circ}\text{C}$ . The dephosphorization rate increases from 86 % to 98 % with the roasting temperature increasing from 1 300  $^{\circ}\text{C}$  to 1 400  $^{\circ}\text{C}$ . However, it increases only 1% from 1 400 to 1 500  $^{\circ}\text{C}$ . This suggests that most of phosphorus has been removed at 1 400  $^{\circ}\text{C}$ , and the temperature is one of the main factors to affect dephosphorization efficiency of the monazite.

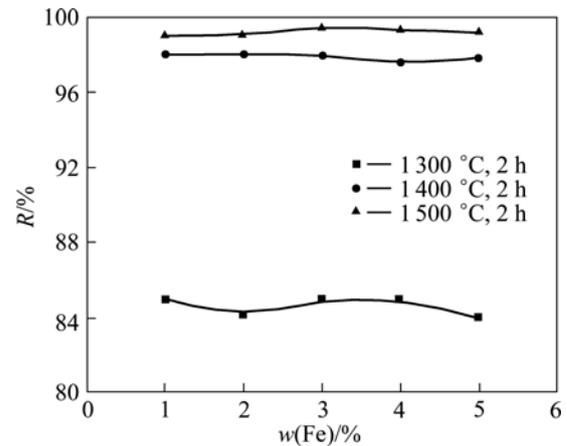


Fig.4 Influence of Fe mass fraction on dephosphorization rate of monazite under different conditions

Fig.5 illustrates the effect of  $\text{Fe}_2\text{O}_3$  on the dephosphorization efficiency of the monazite with charred coal, where the particle sizes of the monazite and charred coal are 75 and 150  $\mu\text{m}$ , respectively. It can be found that  $\text{Fe}_2\text{O}_3$  has no obvious effect on the dephosphorization efficiency under the conditions investigated, which is similar to Fe. However, the roasting temperature has a great impact on the dephosphorization efficiency of the monazite.

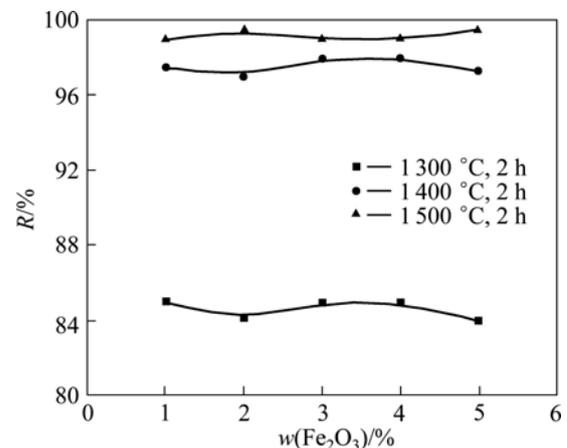
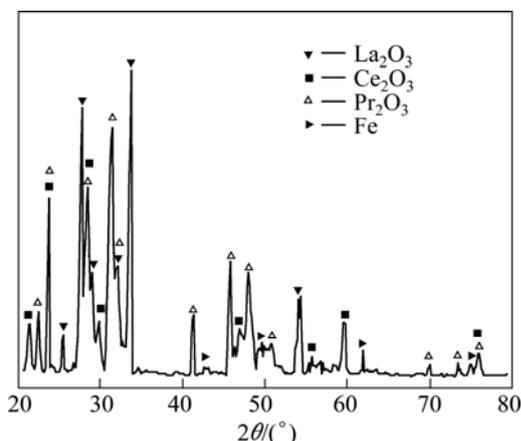


Fig.5 Influence of  $\text{Fe}_2\text{O}_3$  content on dephosphorization rate of monazite

Fig.6 shows the XRD pattern of the monazite pellets roasted at 1 500  $^{\circ}\text{C}$  for 2 h, where 5%  $\text{Fe}_2\text{O}_3$  has been added to the monazite pellets. No diffraction peaks of  $\text{REPO}_4$  have been found on the XRD pattern, suggesting that all of the  $\text{REPO}_4$  have been reduced to  $\text{REO}$ . Meanwhile, no  $\text{Fe}_2\text{O}_3$  has been found in the limitation of XRD, while only a small amount of Fe has been found. At the temperature over 1 000  $^{\circ}\text{C}$ , carbon exists in the systems as  $\text{CO}$ . According to thermodynamics calculation,  $\text{Fe}_2\text{O}_3$  in the systems will be reduced to Fe by  $\text{CO}$  at temperature higher than 710  $^{\circ}\text{C}$ . This is the

reason why there is no  $\text{Fe}_2\text{O}_3$  detected in XRD patterns. Therefore, the effect of  $\text{Fe}_2\text{O}_3$  on the dephosphorization efficiency in the temperature region is the same as Fe. It also can be found that Fe has no obvious effect on the carbon thermal reduction of  $\text{REPO}_4$ , and does not react with P to form any compounds.



**Fig.6** XRD pattern of pellet of monazite mixed with 5%  $\text{Fe}_2\text{O}_3$  after roasting at 1 500 °C for 2 h

#### 4 Conclusions

1) The charred coal is an effective candidate for removing phosphorus to form monazite. There is large dephosphorization efficiency when the roasting temperature is between 1 200 and 1 400 °C. The dephosphorization rate reaches 98 % when the pellets of the monazite and charred coal are roasted at 1 400 °C for 2 h.

2) The roasting temperature is the main factor influencing the dephosphorization efficiency of the monazite using the charred coal, and the roasting time has less effect on it.

3) When the particle size of the monazite is 75  $\mu\text{m}$ , the particle size of the charred coal has a significant influence on the dephosphorization efficiency of the monazite. High dephosphorization efficiency can be reached only when the particle size of the charred coal is about 150  $\mu\text{m}$ .

4) Fe and  $\text{Fe}_2\text{O}_3$  have no obvious effect on the dephosphorization efficiency of the monazite using the charred coal when the temperature is lower than 1 500 °C.

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(Edited by LI Xiang-qun)