Thermogravimetric Analysis of Hercynite Synthesized by Reaction Sintering

Junhong Chen, Mingwei Yan*, Jindong Su, Bin Li, WenjunMi&Jialin Sun

University of Science and Technology Beijing, Beijing 100083, China

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Abstract. The hercynite synthesized at 1600°C in protection atmosphere was thermogravimetrically analyzed. The results show that the change of oxygen partial pressure during sintering transforms some Fe$^{2+}$ in the hercynite crystal structure into Fe$^{3+}$ but the hercynite structure remained. Based on the modal for hercynite with Fe$^{3+}$ given by Dehe, et al., the structural formula was calculated as $Fe^{2+}_{0.49}Fe^{3+}_{0.355}Al^{3+}_{1.142}Fe^{2+}_{0.503}Fe^{3+}_{0.355}Al^{3+}_{1.142}O_{4}$.

1 INTRODUCTION

In recent years, hercynite as a new environmental friendly chrome-free refractory has drawn much attention from researchers worldwide [Liu Huilin,2003] [Zhang Junbo,2007] [MaShulong,2011] [Chen Junhong,2011]. Liuet al. synthesized hercynite by reaction sintering using special grade bauxite and iron scale as raw materials and studied the influence of the reduction atmosphere and sintering temperature on synthesis[Liu Huilin,2003]. Zhanget al. investigated the effects of raw materials and synthesis methods on the synthesis of hercynite using Fe2O3 powder, iron scale and Al2O3 powder as raw materials [Zhang Junbo,2007]. Maet al. discussed the effect of oxygen partial pressure on the synthesis of hercynite using Fe2O3 powder, α-Al2O3 powder and graphite powder as raw materials, and thermodynamically calculated the suitable synthesis temperature and oxygen partial pressure in nitrogen atmosphere to prove the feasibility[Ma Shulong,2011]. Chen et al. synthesized hercynite by reaction sintering using industrial alumina and iron scale as raw materials, and sintering in nitrogen atmosphere or in carbon reduction condition [Chen Junhong,2011].

Whereas, in refractories field, a very few researchers studied the structural formula of their synthesized hercynite. As known, hercynite (FeAl2O4) has a positive spinel structure at room temperature under normal pressure, Fe and Al orderly occupy the tetrahedron position and octahedron position, respectively. However, at high temperatures, the distribution of Fe and Al in the two positions becomes orderless. Therefore, the hercynite synthesized at high temperatures is not the theoretical FeAl2O4. Harrison et al. gave the structural formula $Fe^{2+}_{x}Al^{3+}_{y}(Fe^{3+}_{x}Al^{3+}_{y})O_{4}$ on condition that Fe$^{3+}$ transforms completely into Fe$^{2+}$[Harrison Richard J, 1998]. Dehe et al. gave the formula $Fe^{2+}_{x}Fe^{3+}_{1-x}Al^{3+}_{y}$ on condition that the synthesized hercynite only has a single phase and Fe$^{3+}$ exists[Dehe. G,1975]. Thus, in this work, hercynite was synthesized by reaction sintering in protection atmosphere at 1600°C using analytically pure iron oxide, analytically pure alumina and graphite as raw materials, and the structure of the synthesized hercynite was analyzed by a high-precision thermogravimetric analyzer.

2 EXPERIMENTAL

2.1 Preparation of hercynite specimen

Analytically pure ferro oxide (ω(Fe2O3) > 99.2%), Analytically pure alumina (ω(Al2O3)>99.5%), and graphite powder (ω(C)>99.5%) were batched at the Fe2O3: Al2O3: C ratio of 43: 57: 3, added with dextrin as binder, milled in a planetary ball miller with absolute ethyl alcohol as medium for 4h. The airdried mixture was then pressed into columns with sizes of
Ø25mm×35mm under 10MPa.

The green specimens were sintered at 1600°C for 4h in protection atmosphere.

2.2 Tests of synthesized hercynite specimen

The phase composition of the sintered specimen were characterized by a Rigaku D/Max 2200PC X-ray diffractometer (CuKα radiation, Ni filter, λ=0.15406nm, voltage=40kV, current=150mA, scanning speed=10°/min, and 2θ=10–90°). The microstructure of the sintered specimen was characterized by a FEI scanning electron microscope equipped with an energy dispersive spectroscopy (Oxford).

The synthesized hercynite was crushed and milled into powders finer than the 225 mesh powder. The obtained powder was put into an Al2O3 crucible and then the thermogravimetry test was carried out in compressed air with 21% of oxygen content at a flow rate of 30mL/min with a temperature rising rate of 5K/min. The TG curve was recorded by a computer automatically.

Nezsch STA409C thermogravimetric analyzer produced in Germany was adopted in this work. Its maximum testing temperature is 1873K and the maximum rising rate is 50K/min. The sensitivity of the balance is 0.0001mg.

3 RESULTS AND DISCUSSION

3.1 XRD, SEM and EDS

Figure 1 shows the XRD patterns of the sintered specimen and the theoretical hercynite. It is found that the sintered specimen has the same diffraction peaks with the theoretical hercynite, indicating that the obtained specimen has the same structure with the theoretical hercynite. Figure 2 shows the SEM images of the sintered specimen. A homogenous morphology is observed. Thus, combining the XRD, SEM and EDS results, it is believed that the sintered specimen has a single phase of hercynite structure.

Figure 1. XRD pattern of sintered specimen
3.2 Thermogravimetry test

The TG curve of the sintered specimen is shown in Figure 3. As temperature rises, the mass keeps rising and tends to stable at 1000°C. When the specimen is completely oxidized, the mass is unchanged, reaching the maximum mass gain of 4.18322%.

![Figure 3. TG curve of sintered specimen](image)

3.3 Discussion

As a reagent for the synthesis of hercynite, FeO has different oxygen partial pressure ranges for its stability at different temperatures. On the basis of Fe-O oxygen potential diagram [Chen Zhaoyou, 2005], a synthesis atmosphere is selected. As shown below, at 1600°C, reaction (1) has $\Delta G < 0$, proving the feasibility of the hercynite synthesis. The XRD and SEM results confirm that the sintered specimen has a single homogenous hercynite phase.

$$FeO(l) + Al_2O_3(s) = FeO\cdot Al_2O_3(s)$$

$$\Delta G = -71086 + 11.89T$$

(1)

At high temperatures, the cations in hercynite distribute without order, and the structural formula is $Fe^{2+}Al^{3+}(Fe^{3+}Al^{3+})O_4$. The oxidation reaction equation is shown as follows.

$$Fe^{2+}Al^{3+}(Fe^{3+}Al^{3+})O_4 + O_2 \rightarrow Fe_2O_3 + 2Al_2O_3$$

The calculated mass gain of hercynite is $\Delta m/m = 4.5977$, higher than the actual one 4.18322, which means that the sintered specimen has a certain amount of Fe⁺ exist in it. The Fe⁺ in the hercynite is mainly caused by the oxygen partial pressure rise during temperature drop or holding. With the rise of oxygen partial pressure, the oxygen in the atmosphere reacts with hercynite and
enters the hercynite lattice. The following defects reaction will happen: 

\[
\frac{1}{2} O_2 = 2 h^* + O_{o}^* + V_{Fe}^* ,
\]

where, \( h^* \) is the electron hole. The delocalization movement improves the oxidation of Fe2+ into Fe3+. Since the amount of Fe3+ is not enough for the hercynite to decompose into two phases, the sintered specimen has a single phase of the structure of hercynite, as proved by Figure 1.

[Dehe. G, 1975] has given the structural formula of hercynite which contains Fe3+: 

\[
Fe^{2+}_{0.541}Fe^{3+}_{0.297}Al^{3+}_{0.162}\left[Fe^{2+}_{0.499}Fe^{3+}_{0.298}Al^{3+}_{1.244}\right]O_4 \quad (\eta=0.115; \lambda=0.385 \ x=0.497).
\]

Based on this formula and the data in Figure 3., the formula of the obtained hercynite is calculated as 

\[
Fe^{2+}_{0.497}Fe^{3+}_{0.355}Al^{3+}_{1.142}\left[Fe^{2+}_{0.503}Fe^{3+}_{0.355}Al^{3+}_{1.142}\right]O_4 .
\]

4. CONCLUSION

The hercynite synthesized at 1600°C in protection atmosphere was thermogravimetrically analyzed. The results show that the change of oxygen partial pressure during sintering transforms some Fe2+ in the hercynite crystal structure into Fe3+ but the hercynite structure remained. Based on the modal for hercynite with Fe3+ given by Dehe, et al., the structural formula was calculated as 

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Fe^{2+}_{0.497}Fe^{3+}_{0.355}Al^{3+}_{1.142}\left[Fe^{2+}_{0.503}Fe^{3+}_{0.355}Al^{3+}_{1.142}\right]O_4 .
\]

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Author to whom correspondence should be addressed e-mail: dabaiel23@126.com (Mingwei Yan); Tel: +86 17701121103

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