Thermogravimetric Analysis of Hercynite Synthesized by Reaction Sintering

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Abstract. The hercynite synthesized at 1600C in protection atmosphere was thermogravimetrically analyzed. The results show that the change of oxygen partial pressure during sintering transformssome Fe^{2+} in the hercynitecrystal structure into Fe^{3+} but the hercynitestructure remained. Based on the modal for hercynite with Fe^{3+}given by Dehe, *et al.,* the structural formula was calculated as $Fe^{2+}_{0.497}Fe^{3+}_{0.355}Al^{3+}_{0.148}[Fe^{2+}_{0.503}Fe^{3+}_{0.355}Al^{3+}_{1.142}]O_4$.

1 INTRODUCTION

In recently 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 her cynite 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 Al2O3powder 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]. Chenet 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 becomesorderless. Therefore, the hercynite synthesized at high temperatures is not the theoretical FeAl2O4. Harrison et al.gave the structural formula $Fe^{2+}_{1-x}Al^{3+}_{x}(Fe^{2+}_{x}Al^{3+}_{2-x})O_4$ on condition that Fe3+ transforms completely into Fe2+[Harrison Richard J, 1998].Deheet al.gave the formula $Fe^{2+}_{\lambda}Fe^{3+}_{1-\lambda-\eta x}Al^{3+}_{\eta x}[Fe^{2+}_{1-\lambda}Fe^{3+}_{1+\lambda-x+\eta x}Al^{3+}_{(1-\eta)x}]O_4$ on condition that the synthesized hercynite only has a single phase and Fe3+ exists[Dehe. G,1975]. Thus, in this work,hercynitewas synthesized by reaction sintering in protection atmosphere at 1600C using analytically pure iron oxide, analytically purealumina 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 1600C for 4h in protection atmosphere.

2.2 Tests of synthesized hercynite specimen

The phase composition 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 anenergy dispersive spectroscopy (Oxford).

The synthesized hercynite was crushed and milled into powders finer than the 225 mesh powder. The obtained powder was put into anAl2O3crucible and then the thermogravimetry test was carried out in compressed air with 21% of oxygen content at a flow rate of 30mL/min witha temperature rising rate3of 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 specimenandthe 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 morphologyis observed. Thus, combining the XRD, SEM and EDS results, it is believed that the sintered specimen has a single phase of hercynite structure.

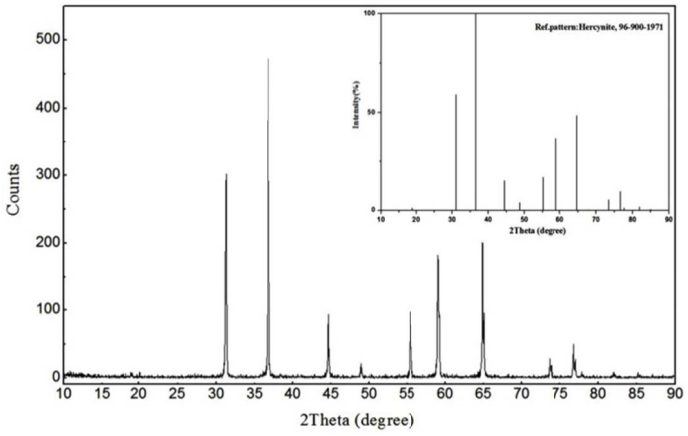
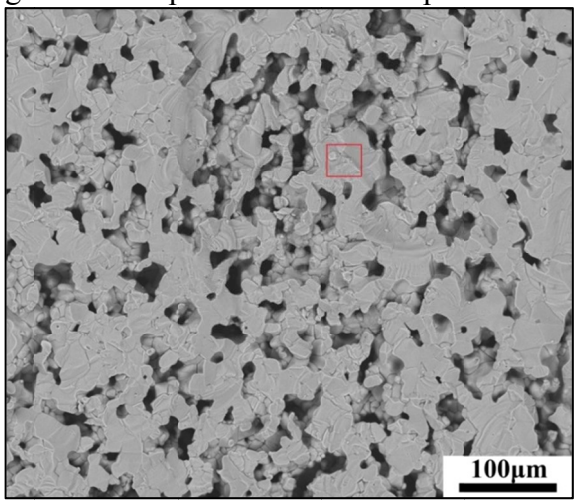


Figure 1.XRD pattern of sintered specimen



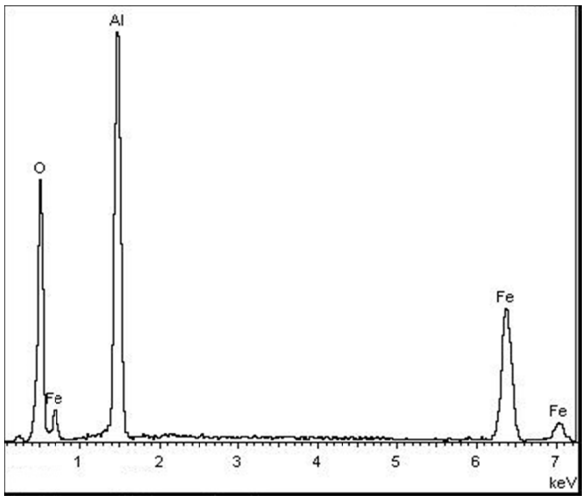


Figure 2. SEM and EDS of sintered specimen

3.2Thermogravimetry 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 1000C. When thespecimen is completely oxidized, the mass is unchanged, reaching the maximum mass gain of 4.18322%.

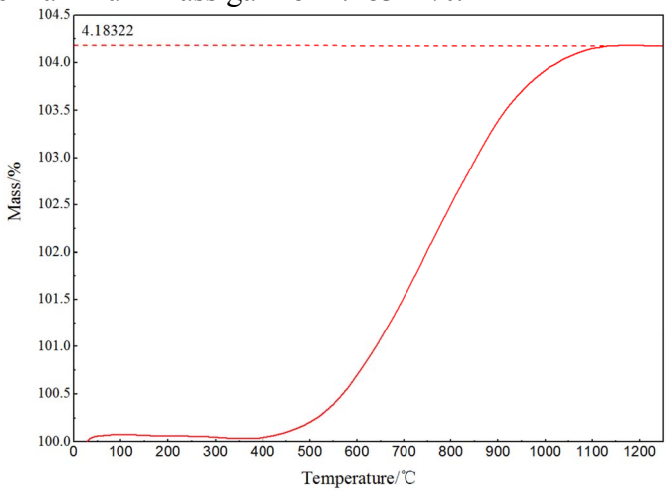


Figure 3.TG curve of sintered specimen

3.3Discussion

As a reagent for the synthesis of hercynite, FeOhas different oxygen partial pressure rangesfor 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 1600C, 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 hercynitephase.

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

$$\Delta G = -71086 + 11.89T \qquad (1)$$

At high temperatures, the cations in hercynite distribute without order, and the structural formula is $Fe^{2+}_{1-x}Al^{3+}_{x}(Fe^{2+}_{x}Al^{3+}_{2-x})O_4$. The oxidation reaction equation is shown as follows.

$$Fe^{2+}_{1-x}Al^{3+}_{x}(Fe^{2+}_{x}Al^{3+}_{2-x})O_4 + O_2 \rightarrow Fe_2O_3 + 2Al_2O_3$$

The calculated mass gain of hercynite is $\Delta m/m=4.5977$, higher than the actual one 4.18322, which means that the sinteredspecimen has a certain amount of Fe3+exist in it. The Fe3+ 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: $\frac{1}{2}O_2 = 2h^{\cdot} + O_o^{x} + V_{Fe}^{''}$, where, $h^{\cdot}$ is the electron hole. The delocalizationmovement improves the oxidation of Fe2+ into Fe3+. Since the amount of Fe3+ is not enough for the hercynite to decompose into two phases, the sinteredspecimenhas a single phase of the structure of hercynite, as proved by Figure 1.

[Dehe. G,1975] has given the structural formula of hercynitewhich contains Fe3+: $Fe^{2+}_{0.541}Fe^{3+}_{0.297}Al^{3+}_{0.162}[Fe^{2+}_{0.459}Fe^{3+}_{0.298}Al^{3+}_{1.244}]O_4$ (η=0.115; λ=0.385 x=0.497). Based on this formula and the data in Figure 3., the formula of the obtained hercynite is calculated as $Fe^{2+}_{0.541}Fe^{3+}_{0.297}Al^{3+}_{0.162}[Fe^{2+}_{0.459}Fe^{3+}_{0.298}Al^{3+}_{1.244}]O_4$.

4.CONCLUSION

The hercynite synthesized at 1600C 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 $Fe^{2+}_{0.497}Fe^{3+}_{0.355}Al^{3+}_{0.148}[Fe^{2+}_{0.503}Fe^{3+}_{0.355}Al^{3+}_{1.142}]O_4$.

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REFERENCES

[1] Liu Huilin et al. 2003 Ren and W. P. Shen. Sintering synthesis of hercynite clinker.*NaihuoCailiao*37(6): 333-335.

[2] Zhang Junbo et al. 2007. Preparation of hercynite.*Bulletin of the Chinese ceramic society* 26(5):1003-1006.

[3] Ma Shulong et al. 2011. Synthesis of hercynite under N_2atmophete.*Journal of the Chinese ceramic society* 39(3):424-429.

[4] Chen Junhong et al. 2011. Synthesis of hercynite by reaction sintering.*Journal of the European Ceramic Society* 31:259–263.

[5] Harrison Richard J. et al. 1998.The temperature dependence of the cation distribution in synthetic hercynite ($FeAl_2O_4$) from in-situ neutron structure refinements.*American Mineralogist* 83:1092-1099.

[6] Chen Zhaoyou. 2005.Formation of ferrous oxide and hercynite. *NaihuoCailiao*, 39(3):207-209.

[7] Dehe.G at al. 1975.Determination of a cation distribution model of the spinel system $Fe_{3-x}Al_xO_4$.*Physica Status Solidi (a)* 31: 439-447.