Effect of SiO₂ addition on the synthesis of hercynite with high purity

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Hercynite as a kind of chrome-free and environmental friendly material is widely investigated. In this work, hercynite with high purity was synthesized using Fe₂O₃ and Al₂O₃ as raw material with SiO₂ addition under controlled temperature and atmosphere system. The phase and microstructure of the obtained product were investigated using XRD, SEM and TEM techniques. The effect of SiO₂ on the synthesis of hercynite with high purity was discussed from both theoretical and experimental aspects. The results show that SiO₂ addition lowers the formation temperature of the liquid phase, which promotes Al₂O₃ to melt into the liquid phase and makes the formation of hercynite possible during the heating stage. During the process of crystallization, SiO₂ further facilitates the formation of hercynite by the peritectic reaction. During the fast cooling stage, SiO₂ in the form of amorphous silicate exists between hercynite crystals. Therefore hercynite with high purity and dense structure is successfully synthesized. It also shows that 1 mass % SiO₂ addition can effectively promote the crystal growth of hercynite and thus lead to dense structure.

Key-words : Hercynite, High purity, SiO₂ addition, Formation mechanism

1. Introduction

Magnesia chrome bricks have been widely used in cement rotary kilns because of their excellent properties. However, toxic Cr VI brings severe environmental pollution. Recently, attention has been focused on the development of chrome-free refractory to replace magnesia chrome bricks. Among these chrome-free refractories, magnesia-hercynite brick is outstanding based on its excellent coating formation ability, good structure flexibility and stress buffering capacity. Therefore it is a kind of promising material and has been successfully applied at the burning zone of rotary kiln. However production and application of magnesia-hercynite brick in large scale has been rigidly restricted due to the synthesis of hercynite (FeAl₂O₄). The main reason is that the valence state of iron in hercynite is ferrous (Fe²⁺). While generally the stable valence of iron is trivalent. In addition, FeO doesn’t exist below 570°C and be stable within a relatively narrow oxygen partial pressure range. Therefore magnetite and ferric oxide is usually used as raw material to synthesize FeO·Al₂O₃. During the synthesis process, Fe³⁺ can be completely transformed into FeO·Al₂O₃ by effectively controlling the reaction atmosphere and sintering technology. Otherwise Fe, magnetite or residual Al₂O₃ is present in the resultant production. Therefore producing hercynite with high purity as well as good crystal growth has been a long-standing problem.

Researchers have carried out various methods and mainly focused on controlling atmosphere and reaction interface to synthesis hercynite. Chen et al. obtained hercynite with high purity at 1550°C adopting the reaction sintering method. During the synthesis process, strong reductive atmosphere by embedding specimens in carbon at flowing nitrogen was adopted. Chen et al. also pointed out that the content of carbon should be restrictedly controlled to prevent such impurities as Fe₂O₃ and Fe₃O₄ in the sample. Castillo Rodriguez et al. obtained hercynite nanoparticles by pulsed laser ablation in liquid technique. However this method was not suitable for industrialization of hercynite because of its expensive cost. Botta et al. synthesized hercynite at argon atmosphere using Al and Fe₂O₃ while such impurities as Fe, magnetite or hematite remained in the sample. Recently Ma et al. synthesized FeO·Al₂O₃ using Fe₂O₃, α-Al₂O₃ and graphite as raw materials in high pure nitrogen atmosphere and investigated the effect of TiO₂ and SiO₂ addition on hercynite formation. The results indicated that TiO₂ and SiO₂ could generate a simulative significance on hercynite synthesis. However the obtained hercynite was not pure and contained other phases such as corundum. While this provides an effective method to produce hercynite using a simple method. No further systematic work has been carried out on hercynite synthesis using additives. Considering the practical application of magnesia-hercynite brick, it is extremely necessary to synthesize efficiently hercynite with high purity. In this work, hercynite with high purity was prepared using Fe₂O₃, Al₂O₃ and SiO₂ as raw material. The promotion mechanism of SiO₂ on the formation of hercynite was investigated. This will provide the theoretical and experimental basis for industrialized synthesis of high purity hercynite using a simple and efficient method.

2. Experimental procedure

Analytical purity of Fe₂O₃ [ω(Fe₂O₃) > 99.2%], Al₂O₃ [ω(Al₂O₃) > 99.5%] and SiO₂ [ω(SiO₂) > 99.2%] powders were used as raw material. Dextrin was used as the binder. The starting powders [x = ω(SiO₂)/ω(FeO + Al₂O₃)] with different x values (x = 0, 0.01, 0.03, 0.05) (numbered as S-0, S-1, S-3 and S-5) were mixed by ball milling in an alcohol liquid using a planetary ball mill. The mass ratio of FeO to Al₂O₃ is fixed at 40.8:59.2

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according to the theoretical ratio of hercynite. After ball milling at 500 rpm for 48 h, the slurry was dried in air and pressed into the size of $25 \text{ mm} \times 35 \text{ mm}$ under the pressure of 10 MPa. The sample was put into a tube furnace and then heated up to $1600 \degree C$ in two stages. First stage, the sample was heated to $1000 \degree C$ in air. Subsequently, the sample was heated from 1000 to $1600 \degree C$ at the rate of 1.5°C/min in controlled CO/CO$_2$ atmosphere ($p_{CO}/p_{CO_2} = 6–13$) and held for 4 h. During the cooling stage, the furnace was cooled down to room temperature in two stages. First stage, the temperature was cooled down from 1600 to $1200 \degree C$ at the rate of 2°C/min. Finally the furnace was cooled naturally to room temperature. During the whole cooling stage, the atmosphere was in controlled CO/CO$_2$ atmosphere.

The phases were identified by X-ray diffraction (XRD; M21XVHF22, MAC Science, Japan) using Cu Kα radiation in the angular 10–90°. The morphology and composition of the samples were investigated using scanning electron microscopy (SEM, FEI Nova 230 Nano, the Netherlands) and transmission electron microscopy (TEM, HITACHI H8100, Japan). High resolution electron microscopy (HRTEM, JEM 2010, Japan) operating at 200kV was used to characterize the phase and crystal morphology of the products.

3. Theoretical analysis

According to the phase diagram of Fe–Al–O ternary system and Fe–O binary system, FeO just remains stable within a relatively narrow oxygen partial pressure range during the whole temperature range. Therefore it is important to control the reaction atmosphere. In our experiment, the mixture of CO and CO$_2$ with a certain ratio was flowed into a high purity alumina tube furnace during the whole stage aiming at enabling the phase of hercynite stable. In addition, the heating and cooling temperature system was strictly controlled to ensure the reaction to be carried out at an equilibrium state and thus to obtain high purity hercynite. The effect of SiO$_2$ on synthesis of hercynite can be explained according to the phase diagram.

3.1 The sintering promotion effect of SiO$_2$ on hercynite formation

With the addition of SiO$_2$, the reaction is changed from FeO–Al$_2$O$_3$ binary system to FeO–Al$_2$O$_3$–SiO$_2$ ternary one. The possible reactions may occur as follows:\textsuperscript{13,21,22}

\[
\begin{align*}
\text{FeO}(s) + \text{Al}_2\text{O}_3(s) & = \text{FeO-Al}_2\text{O}_3(s) \quad \text{(1)} \\
\Delta G_1 & = -71086 + 11.89T \\
2\text{FeO}(s) + \text{SiO}_2(s) & = 2\text{FeO-SiO}_2(s) \quad \text{(2)} \\
\Delta G_2 & = -36200 + 21.09T \\
2\text{FeO}(s) + 2\text{Al}_2\text{O}_3(s) + 5\text{SiO}_2(s) & = 2\text{FeO-2Al}_2\text{O}_3-5\text{SiO}_2(s) \quad \text{(3)} \\
\Delta G_3 & = -44341 - 554.86T \\
3\text{Al}_2\text{O}_3(s) + 2\text{SiO}_2(s) & = 3\text{Al}_2\text{O}_3-2\text{SiO}_2(s) \quad \text{(4)} \\
\Delta G_{10} & = 8600 - 17.41T
\end{align*}
\]

From the above equations, the reaction Gibbs free energy activation as the function of temperature can be calculated. The results shows that these above reactions can take place below 1000°C. This was in agreement with the result of Richardson et al.,\textsuperscript{22} who reported that fayalite (2FeO·SiO$_2$) and iron cordierite (2FeO-2Al$_2$O$_3$·5SiO$_2$) could be generated over the temperature range of 850–1000°C. Once 2FeO·SiO$_2$ and 2FeO·2Al$_2$O$_3$·5SiO$_2$ are formed at low temperature, the ternary system of 2FeO-SiO$_2$–2FeO-2Al$_2$O$_3$–5SiO$_2$–SiO$_2$ is built (Fig. 1). Therefore the liquid phase with its composition located in the invariant $d$ is generated at about 1083°C. In addition, since FeO, Al$_2$O$_3$ and SiO$_2$ are dissolving into the liquid phase, the composition point of the liquid phase will change from the invariant point $d$ to the invariant point $e$ where hercynite and some new liquid phase are generated through the following inversion peritectic reaction:

\[
2\text{FeO-SiO}_2 + 2\text{FeO-2Al}_2\text{O}_3-5\text{SiO}_2 \\
\rightarrow L + \text{FeO-Al}_2\text{O}_3
\]

With temperature increasing, the composition of liquid phase goes to the direction of Al$_2$O$_3$ content increasing along the
corresponding balance line in Fig. 1. By comparison, the liquid phase in FeO-Al₂O₃ binary system appears at about 1330°C,¹⁵ which is higher than that of the system FeO-Al₂O₃-SiO₂. Therefore addition of SiO₂ greatly decreases the formation temperature of the liquid phase, which may promote sintering synthesis of hercynite in turn.

3.2 The effect of SiO₂ on hercynite synthesis during the process of crystallization

In this work, the composition points of Specimens S-1, S-3 and S-5 are located slightly on the right of ligature between hercynite and SiO₂, where the primary phase is hercynite. When the ternary phase diagram of FeO-Al₂O₃-SiO₂ reaches equilibrium at 1600°C, the composition point of liquid phase is located at f point in Fig. 2 and the balanced solid phases are hercynite and Al₂O₃.

When the synthetic system begins to cool from 1600°C, the balance among liquid phase, hercynite and Al₂O₃ will be broken and the composition point of liquid phase leaves f point accordingly. The composition point of liquid phase is continuously shifting along the congruent melting boundary between hercynite and Al₂O₃. Hercynite and Al₂O₃ are increasingly crystallizing from the liquid phase according to Eq. (6):

\[ L \rightarrow \text{FeO-Al}_2\text{O}_3 + \text{Al}_2\text{O}_3 \]  

(6)

With temperature further decreasing, the composition point of liquid phase arrives at g point of the peritectic boundary between hercynite and Al₂O₃, where part of Al₂O₃ is melt back into the liquid phase and hercynite is produced by Eq. (7):

\[ L + \text{Al}_2\text{O}_3 \rightarrow \text{FeO-Al}_2\text{O}_3 \]  

(7)

When the temperature continuously cools down to 1380°C (h point in Fig. 1), the composition point of the liquid phase moves to the single peritectic h point of the subsystem 3Al₂O₃·2SiO₂-FeO·Al₂O₃-2FeO·2Al₂O₃·5SiO₂, where the rest of Al₂O₃ is melt back into the liquid phase through the following reaction:

\[ L + 3\text{Al}_2\text{O}_3 \rightarrow 3\text{Al}_2\text{O}_3 + 2\text{SiO}_2 + \text{FeO-Al}_2\text{O}_3 \]  

(8)

When temperature arrives at 1210°C, the composition point of the liquid phase is located at the single peritectic m point of the subsystem 3Al₂O₃·2SiO₂-FeO·Al₂O₃-2FeO·2Al₂O₃·5SiO₂, where 3Al₂O₃·2SiO₂ is melt back into the liquid phase and 2FeO·2Al₂O₃·5SiO₂ is generated through the following reaction:

\[ L + 3\text{Al}_2\text{O}_3·2\text{SiO}_2 \rightarrow \text{FeO-Al}_2\text{O}_3 + 2\text{FeO-2Al}_2\text{O}_3·5\text{SiO}_2 \]  

(9)

Below 1200°C, the furnace is cooled down naturally in the experiment. Since the cooling rate is very fast, the liquid phase hardly crystallizes and thus the amorphous phase is formed between hercynite crystals.

4. Results and discussion

4.1 Phase and microstructure characterization

XRD pattern of the obtained products (S-0, S-1, S-3 and S-5) is shown in Fig. 3. It can be seen that the characteristic peaks for all the obtained products are corresponding to that of hercynite. Especially for the sample without SiO₂ addition (S-0), it seems that hercynite with high purity may be also obtained. Further investigation is carried out.

Figure 4 shows SEM images of the fracture surface of the sample without (S-0) and with SiO₂ addition (S-1, S-3 and S-5). It can be seen that the specimen without SiO₂ addition (S-0) exhibits porous structure. The grain size of hercynite is very small. At higher magnification, the hercynite crystal is about 15 μm. In addition, Al₂O₃ particle is also found (Fig. 5). This can be explained according to FeO-Al₂O₃ binary phase diagram (Fig. 6).¹⁵ During the heating stage, the initial liquid phase appears at 1330°C. Since the mass ratio of FeO to Al₂O₃ in the experiment was set as 40.8:59.2, the composition of liquid phase tends to move to the direction of Al₂O₃ content increasing along the corresponding balance line (the red bold line in Fig. 6). When the temperature reaches 1600°C, the balanced phases are the...
liquid phase composed of hercynite and Al$_2$O$_3$ and residual solid Al$_2$O$_3$. In our experiment, the maximum temperature is 1600°C. Therefore Al$_2$O$_3$ cannot completely enter into hercynite during the cooling stage and remains in the product. This has been verified by the SEM result (Fig. 5). Therefore it is difficult for the mixtures of Al$_2$O$_3$ rich composition located in the system FeO–Al$_2$O$_3$ to obtain hercynite with high purity. Since Al$_2$O$_3$ particles are enwrapped by hercynite crystal, the characteristic peaks of Al$_2$O$_3$ for Sample S-0 are not observed as shown in XRD.

By comparison, the specimens with SiO$_2$ addition (S-1, S-3 and S-5) display more compact structure (Fig. 4). The crystal grain size is larger than that without SiO$_2$ addition, i.e. about 30 µm and the crystal is well developed. The above result indicates that SiO$_2$ addition promotes the sintering and crystal growth of hercynite. It can also be seen from Fig. 4 that further increasing the content of SiO$_2$ above 1%, i.e. 3–5% (S-3 and S-5), the promotion effect on the crystal growth was not obvious.

Fig. 3. XRD pattern of the obtained products without and with SiO$_2$ addition.

Fig. 4. SEM images of the fracture surface of the obtained products without and with SiO$_2$ addition.

Fig. 5. SEM images and EDS analysis of the fracture surface of the obtained product without SiO$_2$ addition.
To investigate the state of SiO₂ in the product, TEM image of the synthesized product with 5% SiO₂ addition was carried out as shown in Fig. 7. The inset SAED pattern and HRTEM indicate that an amorphous layer exists between the two crystals. Further EDS analysis shows that the crystal contained the elements of Fe, Al and O, implying the formation of hercynite crystal. While the amorphous layer is mainly composed of Si, Fe, Al and O, indicating the element of Si enters into silicate and predominately exists between hercynite crystals. This is in consistent with the theoretical analysis.

4.2 The formation mechanism of hercynite

From above analysis, the formation mechanism of hercynite with SiO₂ addition can be illustrated in Fig. 8. It can be seen that the reaction system is changed from FeO–Al₂O₃ binary system to FeO–Al₂O₃–SiO₂ ternary one with SiO₂ addition. This makes fayalite (2FeO·SiO₂) and iron cordierite (2FeO·2Al₂O₃·5SiO₂) can be generated over the temperature range of 850–1000°C. Therefore the ternary system of 2FeO·SiO₂–2FeO·2Al₂O₃·5SiO₂–SiO₂ is built, which leads to the liquid phase to be formed and thus hercynite can be synthesized through the peritectic reaction at lower temperature. The formation of liquid phase can promote sintering synthesis of hercynite in turn. During the process of crystallization, the liquid phase can ensure the residual Al₂O₃ to be completely transformed into hercynite by peritectic reaction and FeO·Al₂O₃ with high purity is obtained. Due to the fast cooling rate, SiO₂ mainly exists between hercynite crystals in the form of amorphous silicate. This is in agreement with the theoretical...
analysis.

5. Conclusions

In this work, the effect of $\text{SiO}_2$ on the synthesis of hercynite was investigated from both theoretical and experimental aspects. The phase and microstructure of the specimens were investigated by XRD, SEM and TEM. The conclusions can be drawn as follows:

FeO–$\text{Al}_2\text{O}_3$ binary system is changed to FeO–$\text{Al}_2\text{O}_3$–$\text{SiO}_2$ ternary system with $\text{SiO}_2$ addition. The formation temperature of the liquid phase is lowered and the sintering synthesis of hercynite is also facilitated. Thus hercynite was generated in advance by the inversion peritectic reaction between fayalite and cordierite at about 1080°C. In addition, $\text{SiO}_2$ promotes residual $\text{Al}_2\text{O}_3$ to be completely transformed into hercynite during the process of crystallization.

Based on theoretical analysis, hercynite with high purity is successfully synthesized using $\text{Fe}_2\text{O}_3$ and $\text{Al}_2\text{O}_3$ as raw material with 1–5 mass % $\text{SiO}_2$ added under controlled temperature and atmosphere systems. $\text{SiO}_2$ mainly existed between hercynite crystals in the form of amorphous silicate. 1 mass % $\text{SiO}_2$ addition can effectively promote the crystal growth of hercynite and thus lead to dense structure.

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