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Synthesis of hercynite by reaction sintering

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Abstract

Hercynite was synthesized by a reaction sintering method using industrial alumina, mill scale, and carbon black as starting materials in the presence of nitrogen and solid carbon at high temperatures. Phase and microstructure changes during the synthesis were investigated. The specimen sintered at 1450 °C consisted of hercynite ($FeO{\cdot}Al_2O_3$), Al_2O_3, Fe_2O_3, Fe_3O_4 and others. In contrast, the specimens sintered at 1550 and 1650 °C only showed hercynite phase, which exhibited typical octahedral or cubic structures. The results showed that by controlling the atmosphere and the addition of reactants, the transformation from Fe_3O_4 to FeO was controlled, and the reduction of FeO by carbon was restrained, which extended the temperature range at which FeO could exist stably, thus making it feasible to prepare high-purity hercynite by a reaction sintering method. The firing temperature of high-purity hercynite should be above 1550 °C.

Keywords: Mill scale; Hercynite; Microstructure; Reaction sintering; Refractories

1. Introduction

Refractories for the burning zone of cement rotary kilns are important for the safe operation of the kilns. The refractories should be resistant to chemical attack and be able to tolerate heat stress-induced damage.[1]

Because of their excellent performance, refractories for the burning zone of dry-method cement rotary kilns have primarily used magnesia chrome bricks in the past.[2] However, due to the formation of water-soluble and carcinogenic Cr^{6+} during the production of cement, which severely contaminates water and soil, the use of magnesia chrome bricks is prohibited worldwide.[3] Currently, chrome-free refractories are primarily composed of magnesite dolomite bricks, magnesia alumina spinel bricks, and magnesia–calcia–zirconia bricks. Unfortunately, the properties of these substitutes are inferior to those of magnesia chrome bricks.[4] Therefore, there have been many studies exploring chrome-free substitutes for magnesia chrome brick.

Buchebner et al.[5] developed a magnesia–hercynite brick by introducing $Fe(Mg)O{\cdot}Al_2O_3$ into magnesia-based materials. The brick forms a coating that reduces the chemical attack on the cement clinker when used in cement rotary kilns. Meanwhile, the change in volume and deterioration of properties caused by the transformation from Fe^{3+} to Fe^{2+} are reduced, giving rise to a material with good structure flexibility and an ability to bear stress.[5,6] Thus, magnesia–hercynite has become a promising candidate material for the burning zone of rotary kilns.

The key problem in preparing magnesia–hercynite bricks is the synthesis of hercynite ($Fe_2O_3{\cdot}Al_2O_3$) or the synthesis of the solid solution based on hercynite ($Fe(Mg)O{\cdot}Al_2O_3$). Hercynite, which has the structural formula $A^{2+}B_2{}^{3+}O_4$, has a spinel crystal structure that belongs to the isometric crystal system of the hexoctahedral class. The melting point of hercynite is 1780 °C.[7]

Single-phase hercynite rarely exists in nature. To synthesize hercynite, FeO needs to react with Al_2O_3 in its stable form with the proper temperature and partial pressure of oxygen (p_{O_2}); otherwise, the synthesis of hercynite will fail. Chen et al. calculated the stable range of FeO in the presence of excess solid carbon and oxygen to be at w(CO) 48%–65% and 680–710 °C.[8] Therefore, it is difficult to synthesize high-purity hercynite due to the severe conditions necessary to obtain pure FeO.

At high temperatures, FeO is stable in the presence of molten Fe. RHI Refractories has developed a commercial electric

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melting method based on the above-mentioned mechanism to synthesize $Fe(Mg)O{\cdot}Al_2O_3$.

Compared with the energy-intensive electric melting method, which requires high temperatures and complex equipment, the reaction sintering method is simple and saves energy. However, it is difficult to control the atmosphere of the reaction. To date, there have not been, to our knowledge, any reports regarding the industrialisation of hercynite by a reaction sintering method.

Botta et al. synthesized $FeO{\cdot}Al_2O_3$ in an Ar atmosphere with metal Al and Fe_3O_4 as starting materials; however, Fe, magnesite, or hematite remained in the final product.[9] Liu et al. synthesized $FeO{\cdot}Al_2O_3$ using calcined bauxite, natural diaspore and Fe_3O_4 as starting materials (embedded in carbon), but the presence of impurities, such as Al_2O_3 and Fe_2O_3, remained.[10] Zhang et al. prepared $FeO{\cdot}Al_2O_3$ using analytically pure Al_2O_3, analytically pure Fe_2O_3 and Fe_3O_4 as starting materials (carbon embedded and sintered in air) but only obtained 20% $FeO{\cdot}Al_2O_3$. The majority of the products were composed of Al_2O_3 and Fe, which meant that the main part of the ferric oxide was reduced to Fe.[11] The main issue with this method is that the reaction atmosphere is difficult to control, leading to different forms of iron oxides, which results in the presence of impurities in the final product. Therefore, high-purity hercynite could not be obtained successfully in the reports mentioned above.

In this paper, to obtain high-purity hercynite, the atmosphere and addition of reactants were adjusted to initiate different reactions at different temperatures to ensure complete transformation of Fe_3O_4 to FeO.

2. Experimental

Starting materials of industrial alumina ($w(Al_2O_3)$: 98.8%, 45 μm), mill scale ($w(FeO + Fe_2O_3)$: 94.5%, 45 μm), and carbon black (w (C): 99.0%, 1.8 μm) were mixed using a mass ratio of 102:77:4 with a carboxymethyl cellulose binder and pressed into spherical specimens (30-mm diameters).

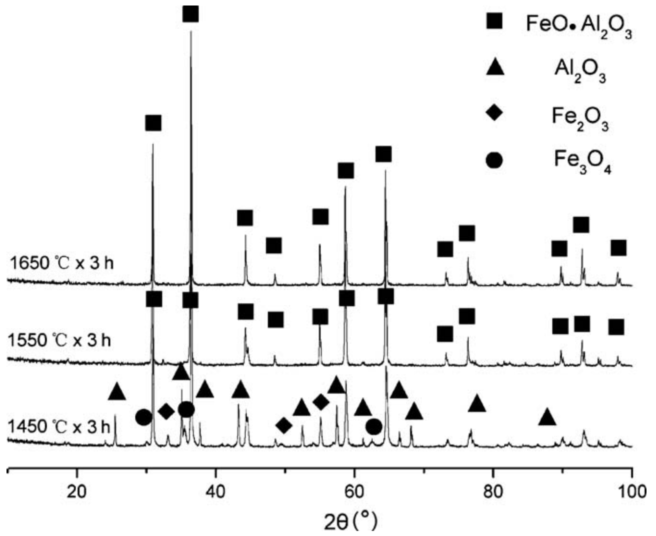

Fig. 1. XRD patterns of the specimens fired at 1450, 1550, and 1650 °C.

The green specimens above were put into a pipe heater and embedded with petro coke (particle size > 10 mm). The petro coke was designed to react with oxygen in the nitrogen gas flow, thereby reducing the oxygen partial pressure. The specimens were then fired for 3 h at 1450 °C, 1550 °C or 1650 °C, respectively, with flowing nitrogen (industrial N_2, 99.5%).

The composition of the specimens was identified by X-ray diffraction (XRD; D/max-RB, Rigaku, Japan) using CuKa radiation ($\lambda = 1.54056$ nm) with a step size of 0.02°. The microstructure was examined by scanning electron microscopy (SEM; Quanta200, FEI, Holland) equipped with energy dispersive spectroscopy (EDS; INCA250 Oxford Instruments, UK).

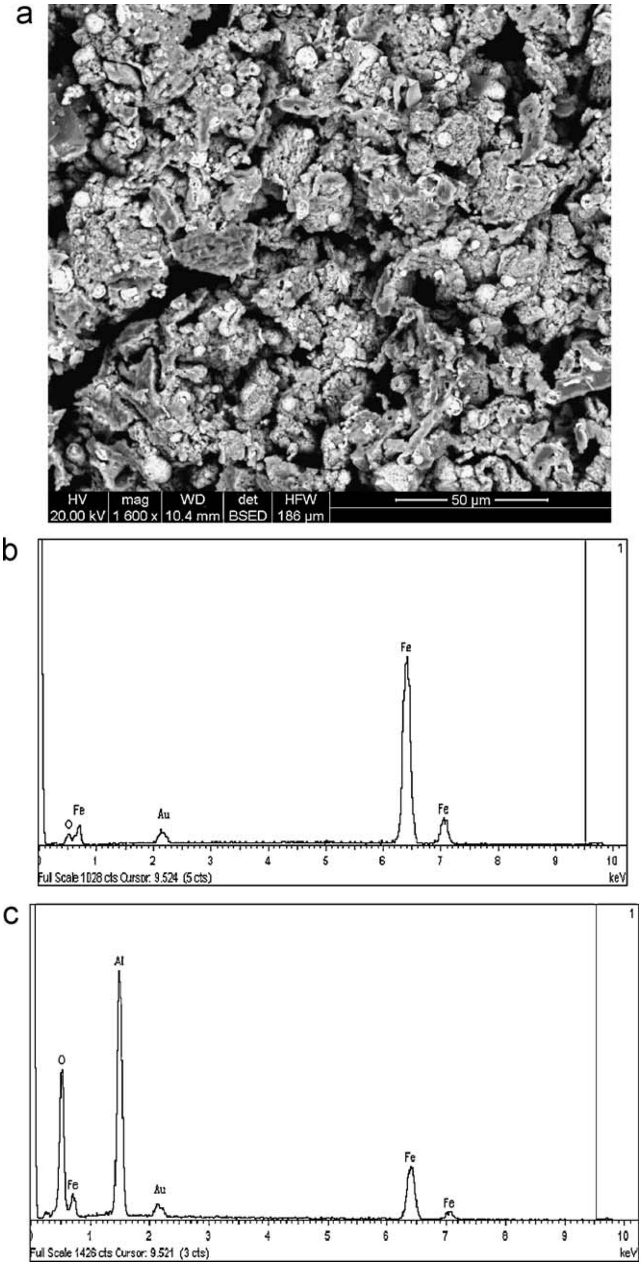

Fig. 2. SEM photograph (a) and EDS patterns (b and c) of the specimen fired at 1450 °C.

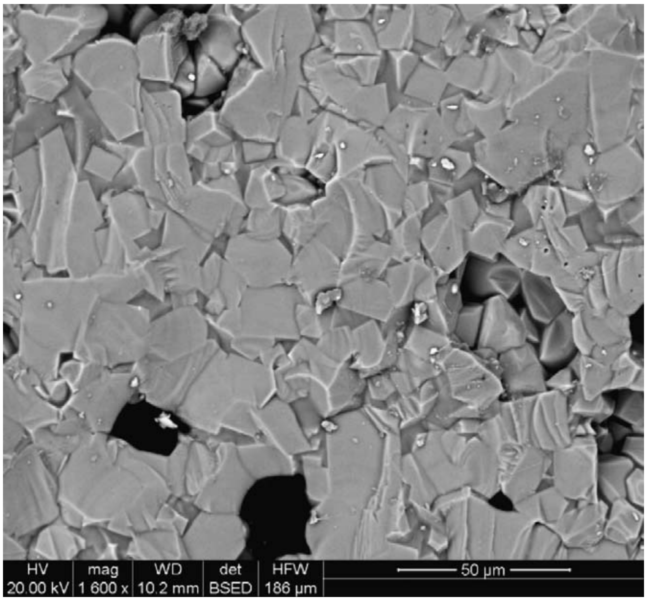

Fig. 3. SEM photograph of the specimen fired at 1550 °C.

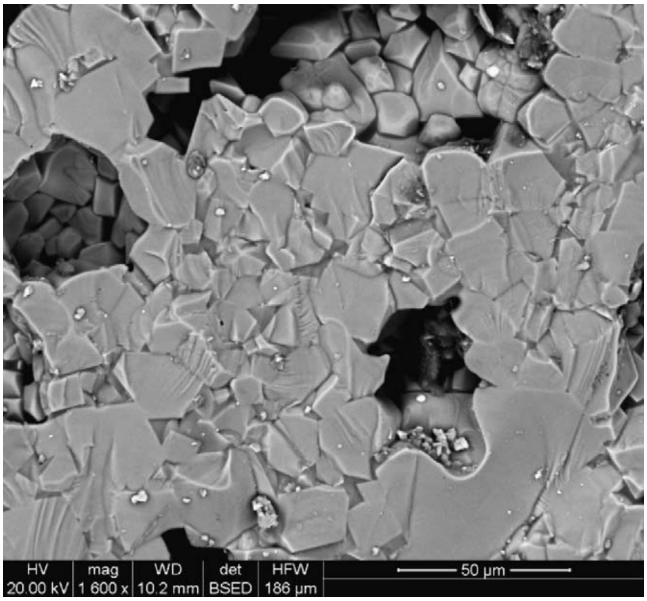

Fig. 4. SEM photograph of the specimen fired at 1650 °C.

3. Results

3.1. XRD analysis

Fig. 1 shows the XRD patterns of the specimens fired at 1450 °C, 1550 °C, and 1650 °C. The specimen fired at 1450 °C mainly consisted of $FeO·Al_2O_3$ (hercynite), Al_2O_3, Fe_3O_4, and Fe_2O_3. The diffraction patterns of the specimens fired at 1550 °C and 1650 °C exhibit the existence of single-phase $FeO·Al_2O_3$, and no impurity peaks are observed, which indicates the starting materials have fully reacted.

3.2. SEM and EDS analysis

The microstructure morphology of the specimen fired at 1450 °C is shown in Fig. 2a. The specimen contained white particles and did not have a dense structure. According to the EDS analysis, the white spherical particles were Fe_3O_4 or Fe_2O_3 (Fig. 2b), whereas the gray parts were hercynite (Fig. 2c). No octahedral or cubic hercynite was observed.

Figs. 3 and 4 show the morphology of sectioned specimens sintered at 1550 °C and 1650 °C. These specimens had dense structures and well-grown hercynite crystals. The crystal structure of as-prepared hercynite is typically octahedral or cubic after being fired at 1550 °C or above, which is consistent with the crystallisation law of hercynite. The hercynite crystals connected with each other, indicating that the hercynite synthesised using this method was of high purity.

4. Discussion

To make Fe_2O_3 and Al_2O_3 fully react, the suggested molar ratio of Fe^{x+} to Al^{3+} is initially 1:1; then, carbon black is stoichiometrically introduced into the system to reduce Fe^{3+} to Fe^{2+} at a high temperature. Therefore, the required mass ratio of industrial alumina, mill scale, and carbon black is 102:77:4.

When industrial nitrogen (N_2 99.5%, O_2 0.5%, by volume) flows through the pipe furnace with the specimens embedded with petrol coke, the small amount of oxygen in the flowing nitrogen gas reacts with petro coke first, forming CO(g) and CO_2(g), as shown in Reaction (I). Therefore, after the reaction with the petrol coke, the atmosphere is mainly N_2(g), CO(g), and CO_2(g). The following thermodynamic data were gathered from previous reports.[12,13]

$$C(s) + CO_2(g) = CO_2(s) + 2CO(g) \qquad \text{(Reaction I)}$$

$$\Delta_r G^\theta = (166550 - 171.00T) \quad \text{J mol}^{-1}$$

when Reaction (I) is in equilibrium, $\Delta_r G^\theta = 0$, and $T = 973.98$ K, which means that in standard conditions, when the temperature is higher than 973.98 K, Reaction (I) moves forward, and O mainly exists in the form of CO(g). When the atmosphere is in balance,

$$\Delta_r G^\theta = -RT \ln \frac{(P_{CO}/P^\theta)^2}{P_{CO_2}/P^\theta} = RT \ln \frac{P_{CO_2}}{P^\theta} - 2RT \ln \frac{P_{CO}}{P^\theta};$$

therefore,

$$RT \ln \frac{P_{CO_2}}{P^\theta} = 166550 - 171.00T + 2RT \ln \frac{P_{CO}}{P^\theta} \qquad (1)$$

Industrial nitrogen contains 0.5% O_2; hence, after reacting with the petrol coke, the CO content is 1.0%, $P_{CO} = 0.001$ MPa, and $P_{CO}/P^\theta = 0.01$. In this atmosphere, Reactions (II)–(VII) may proceed in the specimen, and their $\Delta_r G$ values are calculated by the substitution of Equation 1 due to the existence of solid carbon and the CO–CO$_2$ equilibrium.

$$Fe_3O_4(S) + CO(g) = 3FeO(s) + C_2O(g) \qquad \text{(Reaction II)}$$

$$\begin{aligned}
\Delta_r G &= \left(31391 - 40.08T + RT \quad \ln \frac{P_{CO_2}}{P_{CO}}\right) \quad \text{J mol}^{-1} \\
&= \left(31391 - 40.08T + 166550 - 171.00T + 2RT \quad \ln \frac{P_{CO}}{P^{\theta}} - RT \quad \ln \frac{P_{CO}}{P^{\theta}}\right) \quad \text{J mol}^{-1} \\
&= \left(197941 - 211.08T + RT \quad \ln \frac{P_{CO}}{P^{\theta}}\right) \quad \text{J mol}^{-1} \\
&= (197941 - 249.37T) \quad \text{J mol}^{-1}
\end{aligned}$$

$$FeO(S) + CO(g) = Fe(s) + C_2O(g) \qquad \text{(Reaction III)}$$

$$\begin{aligned}
\Delta_r G &= \left(-21335 + 22.68T + RT \ln \quad RT \ln \frac{P_{CO_2}}{P_{CO}}\right) \quad \text{J mol}^{-1} \\
&= \left(-21335 + 22.68T + 166550 - 171.00T + RT \quad \ln \frac{P_{CO}}{P^{\theta}}\right) \quad \text{J mol}^{-1} \\
&= \left(145215 - 148.32T + RT \quad \ln \frac{P_{CO}}{P^{\theta}}\right) \quad \text{J mol}^{-1} \\
&= (145215 - 186.61T) \quad \text{J mol}^{-1}
\end{aligned}$$

$$Fe_3O_4(S) + C(s) = 3FeO(s) + CO(g) \qquad \text{(Reaction IV)}$$

$$\begin{aligned}
\Delta_r G &= \left(197941 - 211.08T + RT \ln \frac{P_{CO}}{P^{\theta}}\right) \quad \text{J} \times \text{mol}^{-1} \\
&= (197941 - 249.37T) \quad \text{J} \times \text{mol}^{-1}
\end{aligned}$$

$$FeO(S) + C(s) = Fe(s) + CO(g) \qquad \text{(Reaction V)}$$

$$\begin{aligned}
\Delta_r G &= \left(145215 - 148.32T + RT \ln \frac{P_{CO}}{P^{\theta}}\right) \quad \text{J mol}^{-1} \\
&= (145215 - 186.61T) \quad \text{J mol}^{-1}
\end{aligned}$$

$$Al_2O_3(S) + FeO(s) = FeO{\cdot}Al_2O_3(s) \qquad \text{(Reaction VI)}$$

$$\Delta_r G = (-71086 + 11.89T) \quad \text{J mol}^{-1}$$

$$Al_2O_3(S) + Fe_2O_3(s) = Fe_2O_3{\cdot}Al_2O_3(ss) \qquad \text{(Reaction VII)}$$

$$\Delta_r G = (-11.525T) \quad \text{J mol}^{-1}$$

Reactions (II) and (IV) have the same $\Delta_r G$, and Reactions (III) and (V) have the same $\Delta_r G$. Reaction (IV) is the combination of Reactions (I) and (II). Reaction (II) contains a gas-solid reaction (indirect reaction). Reactions (III) and (V) have the same relationship as each other. The relationships between $\Delta_r G$ and the temperatures of Reactions (II)–(VII) are shown in Fig. 5.

As seen in Fig. 5, at high temperatures, $\Delta_r G$ of Reaction (IV) is always lower than that of Reaction (V); hence, Reaction (IV) occurs preferentially, generating the desired FeO.

With the ratio of mill scale to carbon black of 77:4, creating a 1:1 molar ratio of Fe$_3$O$_4$ to C, the carbon black is depleted only during Reaction (IV). When Reaction (IV) is completed, no more Fe^{3+} exists in the system, leading to the occurrence of Reaction (VI) to form hercynite.

In this work, the addition of carbon is the key factor affecting the phase composition of the system. When the concentration exceeds 2%, Fe will be reduced; otherwise, Fe$_3$O$_4$ will remain.

From the binary phase diagram of FeO–Al$_2$O$_3$,[14] the lowest eutectic point of the solution is at 1603 K, which is relatively low and helps the hercynite to grow rapidly and crystallise. As shown in Fig. 1, hercynite, along with other phases, formed in the specimen fired at 1450 °C. In contrast, in the specimens fired at 1550 °C and 1650 °C, hercynite was the only phase, which indicates that for this experiment, a high temperature was favourable for the formation of FeO·Al$_2$O$_3$.

It can be seen in Fig. 2 that in the specimen fired at 1450 °C, the starting materials did not fully react, leaving Al$_2$O$_3$ and Fe$_3$O$_4$ in the specimen. When the temperature was increased to 1550 °C and above, the liquid phase in the specimens

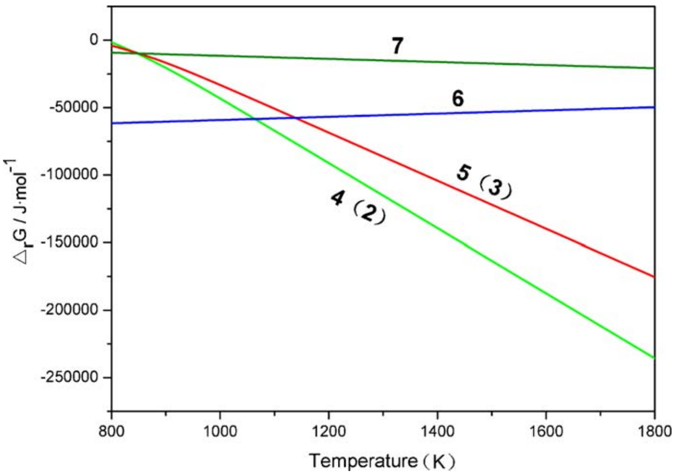

Fig. 5. Relationships between $\Delta_r G^{\theta}$ and the temperatures of Reactions (II)–(VII).

increased, which accelerated the reactions and boosted the crystallisation of hercynite. As shown in Figs. 3 and 4, hercynite particles are in contact with each other directly, indicating high-purity.

5. Conclusions

Hercynite can be prepared by a reaction sintering method using starting materials of industrial alumina, mill scale, and carbon black with a controlled atmosphere and controlled reactants addition. The presence of impurities was observed in the obtained product when fired at 1450 °C because the starting materials had not fully reacted. However, the specimens fired above 1550 °C consisted of high-purity and well-crystallised hercynite.

The synthesis of hercynite by the reaction sintering method in a nitrogen atmosphere with specimens embedded in carbon is not only feasible but also easy to control and operate.

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