Formation of Spinel–Carbon Composite Clinker

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A spinel–carbon clinker has been prepared through a two-step heating process of MgO–Al compact in CO atmosphere. Al partially changes into intermediate phases during low temperature heating step. The phases further react with MgO and CO during high temperature heating step to form spinel and carbon. The precipitated carbon phase is almost amorphous and finely distributed throughout the spinel phase. Because of its low degree of crystallinity, the precipitated carbon shows an oxidation resistance lower than graphite. At higher temperatures, the effect of heating in CO gas on the clinker is negligible, but heating in Ar gas strongly reduces the clinker.

1. Introduction

Among potential requirements for shaped and unshaped refractories, monolithic refractories are more greatly used and castables occupy a high percentage of application in the monolithic group of refractory materials. Castable refractories do not require skilled labour for installation and more easily exhibit their designed characteristics than other types of monolithic refractories such as plastic, ramming and gunning materials. Definitive substitution of refractory bricks by monolithics in steel-ladle lining is hindered by lack of appropriate refractory castables at slag line. In this regard, hydration of magnesia fine grains is a major obstacle of magnesia refractories. The most common rout to overcome this problem is spinel participation in the refractory. This spinel phase can be formed through different methods:

(a) Using pre-sintered spinel grains as starting material.
(b) In situ formation of spinel through direct solid-state reaction between magnesia and alumina grains.
(c) In situ formation of spinel through the reaction between Al₂O₃ or MgO grains and Al–Mg alloys.
(d) In situ formation of spinel through the reaction between MgO grains and Al metal.

In this work, formation of spinel–carbon (MgAl₂O₄–C) clinker, for monolithic applications, has been investigated through the latest method (d). In this regard, a mixture of magnesia and aluminium powders is heated in CO atmosphere. Al reduces CO gas to deposit carbon and form intermediate phases such as Al₂C₃ and alumina. Further, they react with MgO to form spinel and carbon. Content of the precipitated carbon in the obtained clinker is about 20 mass%, which is common in carbon containing refractories.

2. Experimental procedure

2.1 Raw materials

Raw materials used in this study were as follows:

(1) Carbon: natural graphite, purity: more than 99%, size: less than 10 μm,
(2) Al: purity: more than 99%, size: less than 10 μm,
(3) MgO: Calcined “Basic Magnesium Carbonate” (4MgCO₃·Mg(OH)₂·5H₂O).

2.2 Clinker formation process

Al (57.3 mass%) and MgO (42.7 mass%) powders were weighted, well mixed in ethanol and uniaxially pressed at 100 MPa to form compacts with diameter of 15 mm and thickness of 10 mm. Then, they were heated in CO gas at various temperatures for 3 h in an alumina tube furnace. As second step, all heated compacts were ground, pressed and heated at 1500°C for 5 h in CO gas. In all runs, CO gas was flowed at a rate of 0.21/min. Weight changes after first and second heating steps were recorded immediately after cooling. Phase composition of the compacts after each heating step was also examined by X-ray diffraction (XRD) test. Thermogravimetric analysis (TGA) was applied to determine content of precipitated carbon in the formed clinker. Micro-images of polished and fractured surfaces of the obtained clinker were observed by optical and scanning electron microscope (SEM), respectively. Element analyses were conducted on the prepared clinker by SEM and electron-probe microanalyzer (EPMA). Finally, lattice parameter of the formed spinel phase in the obtained clinker was measured through XRD-Step Scanning with rotation step of 0.005° and detecting time constant of 4 s in each step.

2.3 Oxidation behaviour of precipitated carbon in the prepared clinker

Oxidation behaviour of precipitated carbon in the obtained clinker was analysed by differential thermogravimetry (DTG) in air. Heating rate was always 10°C/min. For comparison, an unheated mixture, including spinel (80 mass%) and graphite (20 mass%), as reference, was also examined. Pore size distribution of the prepared clinker was measured by a mercury porosimeter.

2.4 Stability of spinel phase and crystallinity of carbon in the prepared clinker at high temperatures in various atmospheres

The prepared clinker was heated in CO gas and Ar gas at 1600°C. Then, their phase composition and spinel lattice parameter were analysed by XRD. DTG was also conducted on the heated clinkers to investigate possible changes of carbon properties.

3. Results and discussion

3.1 Clinker formation process

Assuming Reaction (1), the MgO–Al compact must gain 89.1% weight after heating in CO gas, and final phase composition is supposed to be spinel (79.8 mass%) and carbon (20.2 mass%).

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2Al(l) + 3CO(g) + MgO(s) = MgAl2O4(s) + 3C(s)  

But in practice, the above reaction could not be completed through a single heating process and a large amount of Al4C3 phase remained even after heating at 1500°C. These are confirmed by XRD results in Fig. 1. As Reaction (2) shows, this Al4C3 can be formed through a reaction between the carbon (precipitated in the Reaction (1)) and Al.

4Al(l, g) + 3C(s) = Al4C3(s)  

This intermediate phase should react with MgO to form spinel according to Reaction (3).

Al4C3(s) + 6CO(g) + 2MgO(s) = 2MgAl2O4(s) + 9C(s)  

It may be supposed that formation of a dense layer near the surface of compacts, during heating at high temperature, prevents inward penetration of CO gas and therefore retards the Reaction (3). To make it clear the heated compact at 1500°C was broken into few pieces in order to reveal new surfaces. Then, they were heated again at 1500°C. But, according to XRD result, a high amount of Al4C3 still remained in the sample. This result refutes the above supposition.

To solve all above problems, and in order to increase homogeneity and promote Reactions (1) and (3), the all heated samples were ground (<88μm), pressed and finally heated again at 1500°C in CO gas for 5h as second step. Phase compositions of the compacts after second step heating are presented in Fig. 2. No Al4C3 was detected in the samples that were heated in the first step at 1100°C or above. Figure 3 presents the weight that the compacts gained during each step. Among the first-step heating processes at different temperatures, a maximum weight gain of 53% occurred at 1200°C. Also, the total weight gain of the compact that was heated at 1200°C (in the first step) reached the highest value (80 mass%). In order to interpret the results in Fig. 3, equilibrium partial pressure of gaseous species over condense phases at different temperatures in $P_{\text{CO}} = 0.1$ MPa were calculated from JANAF thermochemical tables and plotted in Fig. 4. Since Al(l), MgO (s), Al4C3(s) and Al2O3(s) are not thermodynamically stable in the system at $P_{\text{CO}} = 0.1$ MPa at mentioned temperatures, partial pressure of gaseous species at $P_{\text{CO}} = 0.1$ MPa at each temperature were calculated through extrapolation method.

When the first-step heating temperature is low (under 1200°C), rate of the Reactions (1) and (2) are low. Therefore, with decrease of heating temperature in the first step, amounts of the formed spinel and intermediate phases (Al4C3 and Al2O3) decrease and consequently amount of the unreacted Al metal increases (Fig. 1) as Fig. 4(a) shows.
P(\text{AlO}) over Al(l) is higher than those over Al\textsubscript{4}C\textsubscript{3}, Al\textsubscript{2}O\textsubscript{3} and MgAl\textsubscript{2}O\textsubscript{4}. Therefore, since content of remaining Al metal, during and after first step heating at lower temperatures, is higher, and its further presence in the second step lasts longer, total amount of vaporized Al\textsubscript{2}O\textsubscript{(g)} will be higher. Some parts of these gases may migrate to the surface of the compacts and then remove from the system without participating in the Reactions (1) and (2) and therefore without resulting in weight gain. As Fig. 2 shows, even after second-step heating, still some Al\textsubscript{4}C\textsubscript{3} remains unreacted. This can also result in lower weight gain in the second step. Vaporization of MgO(s) in the first and second steps can also result in lower total weight gain.

When the first-step heating temperature is high (over 1200°C), higher amounts of Al\textsubscript{4}C\textsubscript{3} (instead of Al\textsubscript{2}O\textsubscript{3}) remain in the compacts (Fig. 1). Therefore, weight gain in the first step decreases with increase of temperature. As Fig. 4(b) shows, partial pressure of Mg(g) over MgO(s) is quite higher than over MgAl\textsubscript{2}O\textsubscript{4}(s), and it increases with increase of temperature. As a result, when the first-step heating temperature increases, higher amounts of Mg(g) may form and escape from the system. This is more noticeable in the first step, because content of unreacted MgO(s) is higher in this step. Therefore, vaporization of MgO(s), during the first step of heating, can explain the decrease of total weight gain (in Fig. 3) with increase of first-step heating temperature over 1200°C.

As a result, the best temperature for the first step of heating can be deduced as 1200°C. Since now, the word clinker will be referred only as the compact that was obtained through two-step heating process at 1200 and 1500°C in the first and second steps, respectively.

TGA result of the obtained clinker in Fig. 5 presents a weight loss of 18.1%. But, according to Reaction (1), carbon content and therefore weight loss of the clinker after oxidation must be 20.2%. For quantitative discussion, the obtained clinker was subjected to element analysis by EPMA. Since the sample was coated by carbon, only Al, Mg and O were quantitatively analysed. The average of results is as follows:

\[
\begin{align*}
\text{Al} &= 38.02 \text{ mass}\%; \quad \text{Mg} = 16.20 \text{ mass}\%; \\
\text{O} &= 45.78 \text{ mass}\% \\
\text{MgO} &= 27.2 \text{ mass}\%; \quad \text{Al}_2\text{O}_3 = 72.8 \text{ mass}\%
\end{align*}
\]

By comparing the above results with normal spinel (MgO = 28.3 mass%; Al\textsubscript{2}O\textsubscript{3} = 71.7 mass%), it may be concluded that some part of MgO escaped from the system during heating (according to Reaction (4) and Fig. 4(b)).

\[
\text{MgO(s)} + \text{C(s)} = \text{Mg(g)} + \text{CO(g)} \quad (4)
\]

But, Reaction (4) alone cannot explain the measured weight gain during heating process (80 mass%) and weight loss during oxidation (18.1 mass%). According to the equilibrium diagram in Fig. 4(a), since Al\textsubscript{2}O\textsubscript{(g)} has the highest partial pressure, its formation through Reaction (5) and further partially escape of it before participating in the Reaction (1) must be also considered.

\[
2\text{Al(l)} + \text{CO(g)} = \text{Al}_2\text{O}_3(g) + \text{C(s)} \quad (5)
\]

Although considering Reaction (5) in addition to Reaction (4) may explain the measured weight loss after oxidation, they still cannot explain the measured weight gain during heating process. Remaining of a little Al\textsubscript{4}C\textsubscript{3} (resulted from Reaction (2)) in the obtained clinker and its oxidation behaviour (Reaction (6)) during TGA analysis, to the accomplishment of the Reactions (4) and (5) can successfully explain all above experimental results and their deviation from the theoretical values.

\[
\text{Al}_4\text{C}_3(s) + 6\text{O}_2(g) = 2\text{Al}_2\text{O}_3(s) + 3\text{CO}_2(g) \quad (6)
\]

Taking Reactions (1), (2), (4), (5) and (6), experimental results of total weight gain during heating process,
weight loss during oxidation in air and element analysis into consideration, we found out that:
- Escaped Al (in the form of $\text{Al}_2\text{O}_3(g)$) and escaped MgO (in the form of $\text{Mg}(g)$) were 0.47 and 2.59 mass%, respectively (according to the total starting weight),
- Final phase composition of the obtained clinker was:
  - Spinel: 78.8 mass%; Carbon: 19.0 mass%;
  - $\text{Al}_4\text{C}_3$: 2.2 mass%

This much $\text{Al}_4\text{C}_3$ (2.2 mass%) was too little to be detected by XRD. As Fig. 2 shows, $\text{Al}_4\text{C}_3$ content in the compacts (after two-step heating process) decreases when first step heating temperature increases from 700 to 900°C. Therefore, remaining of a little $\text{Al}_4\text{C}_3$ in the obtained clinker can be expected.

An optical microscope image of polished surface of the obtained clinker is presented in Fig. 6. The structure is quite porous and maximum size of separated dense area is about 100 $\mu$m. Therefore, after crushing, a fine size clinker can be obtained. SEM pictures of fractured surface of the clinker in Fig. 7 provide clearer images of the clinker grains. As they show, the clinker has a very fine and homogeneous structure. Each clinker grain is made of very fine spinel grains (smaller than 1 $\mu$m) and amorphous carbon. Even through random point-by-point element analysis by EDX-SEM, at high magnification, no points with only pure carbon peak (without Mg and Al peaks) were detected. This verifies a very fine and homogenized distribution of carbon in the clinker structure.

### 3.2 Oxidation property of precipitated carbon in the prepared clinker

XRD patterns of the obtained clinker and the unheated spinel-graphite mixture are presented in Fig. 8. Since carbon peaks in the clinker are quite broad and their intensities are very low, the precipitated carbon must be amorphous. This amorphous carbon is simply expected to show higher oxidation tendency. DTG results of the both samples in Fig. 9 confirm the above statement. The exothermic peak of carbon burnout occurs at 615°C for precipitated carbon in the clinker and at 835°C for crystalline carbon in the spinel-graphite mixture. As TG curves show, oxidation of the obtained clinker starts around 500°C, but graphite burnout starts at higher temperature around 650°C.

It may be supposed that the formed spinel phase can protect carbon from oxidation by surrounding them. To make this clear, two powders with different sizes (Fine: <63 $\mu$m; Coarse: <177 $\mu$m) were prepared by grinding the obtained clinker. Then, they were oxidized in air (by DTG). As results show in Fig. 9, the coarse and fine clinker powders present same oxidation behaviour. This could be expected from SEM pictures in Fig. 7. As this figure shows, the spinel grains are too small (less than 1 $\mu$m) and they are separately distributed in the matrix. Porosimetry analysis in Fig. 10 presents a very fine distribution of open pores among fine spinel grains in the obtained clinker. Therefore,
since the spinel grains do not make an impermeable and continuous framework, they cannot protect carbon from oxidation and their surrounding effect around precipitated carbon must be negligible.

3.3 Stability of spinel phase and crystallinity of carbon in the prepared clinker at high temperatures in various atmospheres

XRD patterns of the obtained clinker before and after heating at 1600°C for 4 h in CO gas and in Ar gas are presented in Fig. 11. After reheating in CO gas, spinel was still the only crystalline phase, and its peaks sharpened a little, resulted from grain growth. XRD Step-Scanning result of spinel peak (reflected from (311) plane), on the basis of Scherrer equation, showed that spinel crystallites in the obtained clinker grew about 6.7% after heating in CO gas at 1600°C for 4 h.

Scherrer equation: \[ t = \frac{k\lambda}{\beta \cos \theta_b} \]

\( t \): crystallite size, \( \lambda \): wavelength of X-ray beam, \( k \): correction factor (≈1), \( \beta \): breadth of peak at its half maximum intensity, \( \theta_b \): Bragg angle.

Figure 12 indicates that reheating in CO atmosphere does not change the spinel lattice parameter. As DTG results in Fig. 13 shows, reheating in CO gas shifts the exothermic peak to a little higher temperature. This effect might be explained by partially crystallization of precipitated carbon in the clinker during reheating at high temperature in CO gas.9) Figure 14 presents thermodynamical stability of
spinel at different partial pressures of magnesium gas. At \( P_{\text{CO}} = 0.1 \text{MPa} \), spinel is unstable above 1790 K at \( P_{\text{Mg}} \) of \( 10^{-5} \text{MPa} \). This temperature increases with increase of \( P_{\text{Mg}} \). Since no noticeable changes occur on the spinel phase during heating at 1600°C in CO atmosphere, \( P_{\text{Mg}} \) over spinel in this condition must be more than \( 10^{-4} \text{MPa} \).

On the other hand, XRD result of reheated clinker in Ar atmosphere (\( P_{\text{O}_2} \) of about \( 10^{-17} \text{MPa} \)) in Fig. 11 shows an obvious effect on the spinel peaks. Although spinel was still the only detected phase, their peaks broadened obviously, shifted to the higher two theta and their intensities decreased. As Fig. 12 shows, after reheating in Ar, the spinel lattice parameter dramatically decreased down to 0.7966 nm. According to Fig. 15, this lattice parameter is correspondence with an alumina-rich spinel phase containing more than 90 mass% \( \text{Al}_2\text{O}_3 \). EPMA element analysis of the reheated clinker in Ar atmosphere confirmed the above results. Since the sample was coated by carbon, only Al, Mg and O were quantitatively analysed. The analysis indicates an alumina-rich spinel phase containing 94.3 mass% \( \text{Al}_2\text{O}_3 \); \( \text{Al} = 50.28 \text{mass\%}; \text{Mg} = 3.49 \text{mass\%} \)

\[
\begin{align*}
\text{(MgO)} &= 5.7 \text{mass\%}; \\
\text{(Al}_2\text{O}_3) &= 94.3 \text{mass\%}
\end{align*}
\]

Therefore, a large amount of magnesium must be removed from the system during heating in Ar at 1600°C. According to previous literatures, at this temperature, \( P_{\text{Mg}} \) over spinel phase in presence of carbon is about \( 10^{-4} \text{MPa} \). Therefore, in order to explain the above changes in the heated clinker in Ar, stability domains in an equimolecular mixture of MgO and \( \text{Al}_2\text{O}_3 \) at \( P_{\text{Mg}} = 10^{-4} \text{MPa} \) at different \( P_{\text{O}_2} \) and at various temperatures have been calculated (using JANAF data) and presented in Fig. 16. As this figure shows, at 1600°C, when Log (\( P_{\text{O}_2} \)) is between (−15.72) and (−19.99), reduction of spinel takes place according to Reaction (7).

\[
\text{MgAl}_2\text{O}_4(s) = \text{Al}_2\text{O}_3(s) + \text{Mg}(g) + 1/2\text{O}_2(g) \tag{7}
\]

The gaseous Mg may escape from the system, but \( \text{Al}_2\text{O}_3 \) remains in the spinel structure. Therefore normal spinel changes to an alumina-rich spinel. In a normal spinel \( \text{(MgAl}_2\text{O}_4) \) oxygen ions form a face centered cubic (fcc), which in alumina ions occupy one-half of octahedral interstitial sites and magnesium ions occupy one-eighth of tetrahedral sites. When normal spinel is heated at high temperature in above-mentioned reducing atmosphere, this structure changes. During reduction, magnesium evaporation and further its escape from the system, increase \( \text{Al}^{3+} \) in the structure. Then, formation of vacant sites and release of \( \text{O}_2 \) and further its reaction with C to form \( \text{CO} \), maintain electroneutrality in the lattice. In this condition, Al and Mg ions occupy the octahedral and tetrahedral cation sites randomly (Reaction (8)).

\[
\text{Mg}^{2+}(\text{Al}^{3+})_2\text{O}_4 + \text{C} = (\text{Mg}^{2+}\text{Al}^{3+})_2(\text{Al}^{3+}\text{Mg}^{2+}\text{Va})_2\text{O}_4 + \text{Mg}↑ + \text{CO}↑ \tag{8}
\]

These changes in the structure can explain lattice parameter changes of the heated clinker in Ar, as showed in Fig. 12. According to the above mechanism, since diffusion (of \( \text{Mg}^{2+} \)) controls kinetic of the spinel reduction process, a range of solid solution with different alumina content is formed during the limited soaking time. Although this difference is not noticeable, it may have some effects in sub micro scales. In XRD analysis, since position of spinel solid solution peaks changes with increase of alumina content (Fig. 15), formation of the mentioned solid solution range, broadens the spinel peaks in the heated clinker in Ar, as showed in Fig. 11. Therefore, in this case, the Scherrer equation is not applicable.

4. Conclusion

Formation and characterization of spinel–carbon clinker
were investigated and following results were obtained:

(1) The clinker was prepared through two-step heating process of MgO–Al compact in CO atmosphere. Al partially changed into intermediate phases (Al2O3 and Al4C3) at lower temperature heating step. They further reacted with MgO and CO at higher temperature heating step to form spinel and carbon.

(2) The best heating temperatures were found as 1200 and 1500°C in the first and second steps, respectively.

(3) A quantitative calculation according to the related reactions and equilibrium diagrams could successfully explain the experimental results.

(4) The precipitated carbon phase in the obtained clinker (19 mass%) was amorphous and showed lower oxidation resistance than graphite.

(5) Effects of CO atmosphere on the obtained clinker at 1600°C were found negligible.

(6) Heating in Ar gas at 1600°C dramatically changed the clinker structure. These changes were clearly explained by presenting the related reactions and equilibrium diagrams.

References


