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Microwave-promoted burning of Portland cement clinker

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Abstract

A new method of burning Portland cement clinker is studied. The microwave sintering is adopted after the raw meal is heated to certain temperature in an electric furnace. The experimental results show that after the raw meal is heated at a low electric heating temperature (1000–1200 °C) and then further sintered with microwave for 1 to 2 min, Portland cement clinkers can be formed. The f-CaO contents of the clinkers are 1–2%. It has also been found that the higher the temperature of the samples put into the microwave cavity, the shorter the time needed for microwave burning. When the temperature is up to 1300 °C, the sample needs to be heated by microwave for only 40 s, and the f-CaO content decreases to 0.65%. It has been proved by the experiments that (1) the new burning technique can greatly increase the forming speed of Portland cement clinkers, (2) Fe_2O_3 can enhance the microwave clinkering. XRD patterns of the clinkers show that their mineral compositions and the characteristic XRD peaks are similar to those of clinkers by conventional burning method. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Microwave sintering; Portland cement clinker; Forming speed; f-CaO; XRD

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1. Introduction

The application of microwave to ceramics sintering began in the mid-1970s. The first experiment attempt of microwave burning cement clinker was reported by Quéméneur et al. [1,2]. After that, Fang et al. and Li et al. [3,4,5] reported microwave clinkering of ordinary and colored Portland cement and C_3S, and so on. The results showed that microwave could enhance the clinkering. Compared with the conventional fast heating processing in the electric furnace, microwave processing can lower the clinkering temperature by about 100 °C. Fang et al. held [3] that Fe_2O_3 had a better ability of microwave absorption and explained the microwave enhancing effect on its clinkering. In the case of white cement clinkering, the existence of amorphous silica had contributed much to the microwave absorption of the samples and its lowered viscosity led to the enhanced ion diffusion. So the clinkering of white cement was enhanced. The document [5] held that Al_2O_3 enhanced the sintering of C_3S, while Fe_2O_3 did not have this effect. So far, there have not been more reports about microwave clinkering of cement. Even fewer researches have been carried out to study the mechanism of microwave-enhanced clinkering. Moreover, some contradictory experiment appearances have been reported. The above-mentioned microwave clinkering methods are all by microwave heating only. The time needed for microwave heating is quite long (20–30 min). In our study, the industry cement raw meal was burned in microwave cavity. The results showed that the materials were not yet decomposed after being heated for 25 min with microwave and the losses were high, up to 33.48–32.88% (the theoretical losses are 39.78%). Accordingly, sole microwave heating is time-consuming and inefficient and is therefore difficult to achieve in industry.

It is widely acknowledged that microwave–material interaction is related to the material type in the electric field. To a dielectric material that has losses in reality in the electric field, its permittivity is complex, which is composed of a real part (dielectric constant) and an imaginary part (dielectric loss factor). The loss tangent (tan) is commonly used to describe the coupling ability of material–microwave. The larger the loss tangent value; the stronger the coupling ability of material–microwave. Those compounds (SiO_2, Al_2O_3, $CaCO_3$, and so on) that constituted cement raw materials are transparent to micro-

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waves at ambient temperature and hardly absorb microwave. Only when heated to above a critical temperature do their loss tangent values begin to grow larger. Accordingly, we put forward a new burning method: transfer the materials heated to certain temperature in the electric furnace to the microwave cavity to heat. At that time, the materials have had stronger microwave absorption ability, so the cement clinkers can be formed in only 1–2 min. This technique proved to be feasible. As this method needs shorter time for microwave-heating and is quite efficient, it is easy to be achieved in industry. Moreover, this microwave sintering method is likely to push forward the reform of cement clinkering technique. So far, such a cement clinker burning method has never been reported.

2. Experimental

2.1. Raw materials

The raw meal used in the experiments was black raw meal of some kiln work. It contained fuel coal, a little fluorite and gypsum as mineralizer. Its chemical composition is listed in Table 1. Fe_2O_3 used as the additive of microwave absorption was analytical pure reagent.

2.2. Sintering setup

The high temperature furnace for electric heating was a silit rod furnace. The temperature was monitored with double platinum–rhodium thermocouple. Microwave sintering was conducted in a 700 W, 2.45 GHz domestic microwave cavity which was reequipped properly. Its power density was 30 kW/m^3.

2.3. Experimental processing

2.3.1. Preparation of raw meal samples

In order to compare the effect of Fe_2O_3 on the burning, four kinds of raw meals were prepared. They were black raw meal and black raw meals with 1%, 2% and 3%, respectively. Their chemical compositions on ignited basis are given in Table 2.

In order to compare the influence of the states of the raw meal on the microwave absorption of the raw meal, two kinds of specimens (powder and piece) were prepared in each group. The mass of each specimen was 20 g. The powdered samples were prepared by slightly compressing 20 g raw meal powder which was put into a corundum crucible (50 ml). The pieces were prepared as following. The 20-g raw meal powder was put in a void steel mold (∅30 mm) and then compressed with the pressure of 20 kN. The pieces were shaped like cakes. The samples were reserved in the corundum crucible.

Table 1
The chemical composition of the raw meal (%)

	Loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO
Raw meal	39.78	12.31	3.67	2.72	39.13	0.68
Ignited basis	0	20.44	6.09	4.52	64.98	1.13

Table 2
The chemical compositions (%) and ratios on ignited basis of the samples

No.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	KH	SM	IM
1	20.44	6.09	4.52	64.98	1.13	0.932	1.93	1.35
2	20.23	6.03	5.46	64.34	1.12	0.926	1.76	1.10
3	20.04	5.97	6.39	63.71	1.11	0.920	1.62	0.93
4	19.84	5.91	7.30	63.09	1.10	0.914	1.50	0.81

$KH = (CaO - 1.65Al_2O_3 - 0.35Fe_2O_3) \div (2.8 \times SiO_2)$; $SM = SiO_2 \div (Al_2O_3 + Fe_2O_3)$; $IM = Al_2O_3 \div Fe_2O_3$.

2.3.2. Burning

When raw meal in the crucibles were heated to certain temperature in the electric furnace, they were immediately transferred to a microwave cavity to heat with microwaves. The heating temperatures in the electric furnace were 1000, 1100, 1200 and 1300 °C, respectively. It was concluded through many experiments that the time needed for microwave-heating the samples at the above temperatures were 135, 95, 60 and 40 s, respectively. In order to compare the burning effects of sole electric heating, sole microwave heating and the combination of the two methods, piece sample #1 was fired for an hour at 1300 °C in the electric furnace, while #1 and #3 powdered samples were heated for 25 min in the microwave cavity. Thus three sintered samples were obtained.

2.3.3. Free lime content determination

The free lime contents in the clinkers were determined with glycerin–anhydrous alcohol method.

2.3.4. X-ray diffraction analysis

The mineral compositions of the clinkers were determined by XRD on a D/MAX-A diffractometer.

2.3.5. Microscopy observations

The micrographs were observed by a reflector microscope.

3. Results

The determined f-CaO contents of the sintered materials are shown in Table 3

3.1. XRD patterns of clinkers

In the experiments, XRD was adopted to determine the mineral compositions of the clinkers and the adopted samples were #2 samples and contrast samples (Fig. 1).

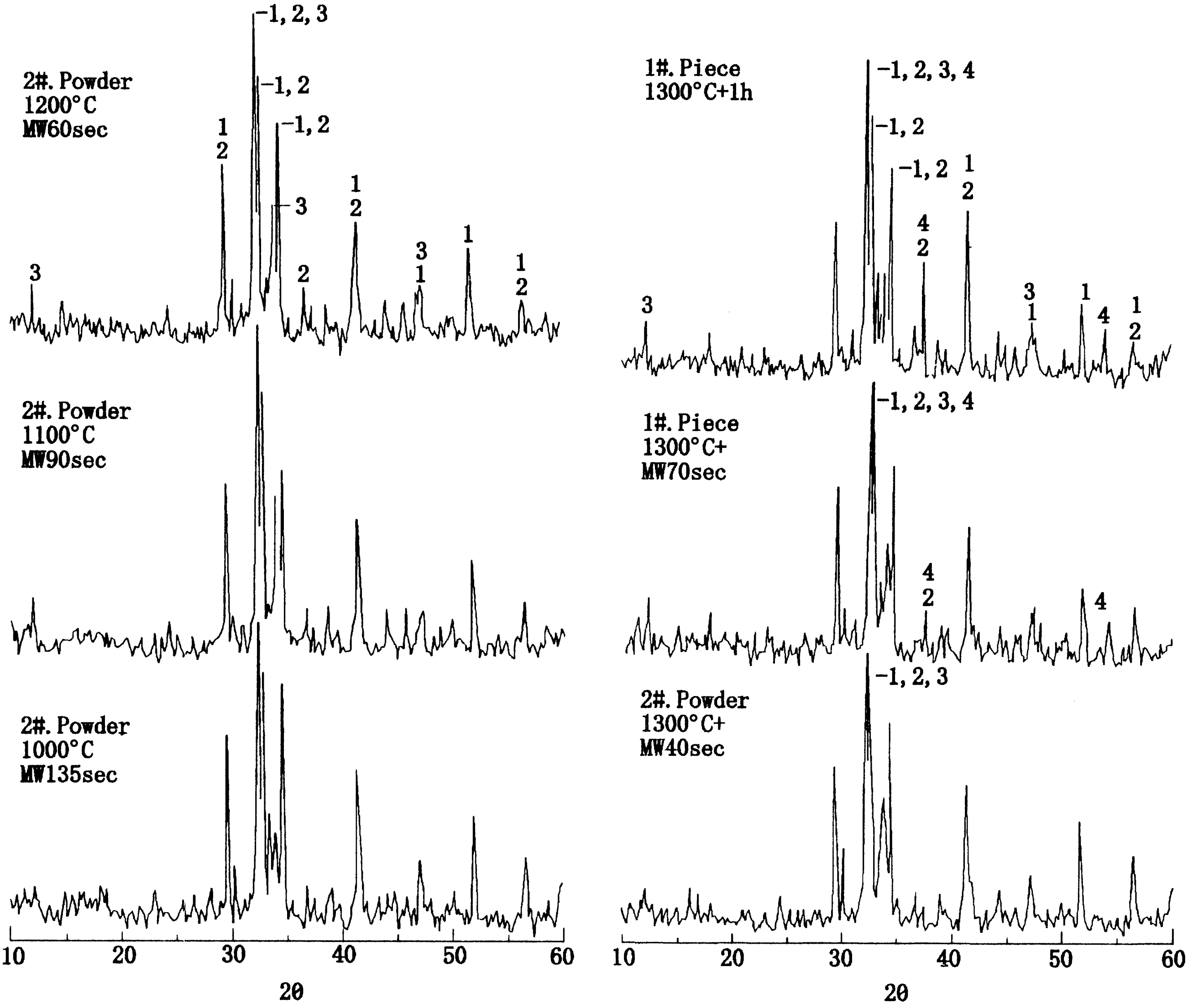

Fig. 1. The XRD patterns of clinkers. (1) C_3S, (2) β-C_2S, (3) C_4AF, (4) CaO.

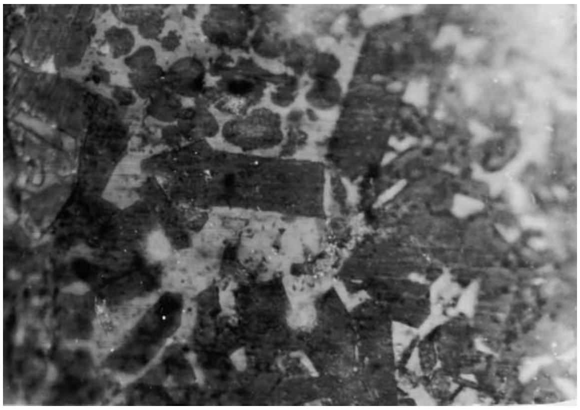

Fig. 2. Mineralogical distribution in clinker that was subjected to electric heating at 1100 °C and microwave heating for 110 s.

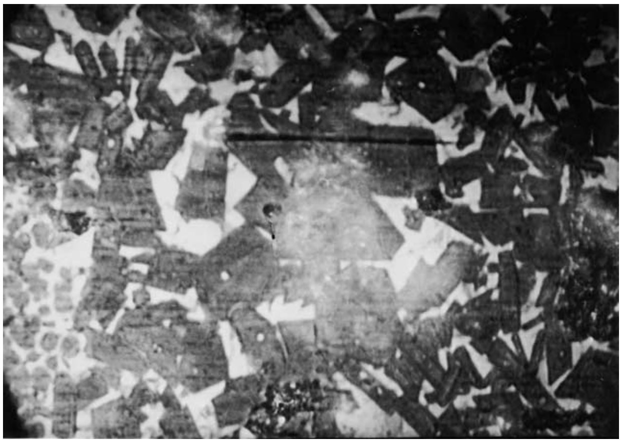

Fig. 3. Mineralogical distribution in clinker which was subjected to electric heating at 1200 °C and microwave heating for 60 s.

3.2. Micrographs of clinkers

In the experiments, two samples (1100 °C + MW110s and 1200 °C + MW60s) of #2 samples (powder) were observed by a reflector microscope (Figs. 2 and 3).

4. Analysis and discussion

In this experiment, it took about 5–10 s to transfer the samples from the electric furnace to the microwave cavity. Owing to radiation of heat during the transferring, the actual temperatures of samples were lower than expected (for example less than 1000 °C, less than 1100 °C, and so on) when the microwave heating was adopted. The higher the electric heating temperature, the faster the radiation, and the more the temperature dropped. Subsequent to this experiment error, the f-CaO content determination results of the sintered samples did not have good regularity. In addition, because the microwave heating time was very short (40–135 s), it was difficult to determine the temperature accurately during the microwave heating. Hence, the microwave burning temperatures were not shown in this experiment.

Table 3 showed that when Sample #1 was heated for 1 h at the temperature of 1300 °C in the electric furnace, its f-CaO content was still at 5.57%. When Samples #1 and #2 were heated from room temperature for 25 min only with microwave, the losses of the samples were high, up to 33.48–32.88%, which were far lower than the theoretical loss (39.78%). Therefore, it can be concluded that $CaCO_3$ in the samples was not yet decomposed completely after being heated for 25 min in the microwave cavity. However, with the new burning method (the combination of electric heating and microwave heating), the f-CaO content of Sample #1 decreased to 3.32% after it was heated to 1100 °C with electric heating and then burned with microwave for 1 min and 45 s. As for Samples #2 and #4, in which Fe_2O_3 was doped, the f-CaO contents decreased to 0.85–2% after they were heated to 1000–1200 °C in the electric furnace and then burned with microwave for only 40–135 s. The results showed that the higher the electric heating temperature; the shorter the time needed for microwave heating.

It is obvious that Fe_2O_3 can enhance microwave clinkering. Compared with Samples #1, #2 and #4 in which Fe_2O_3 was doped had lower f-CaO contents and needed shorter time for microwave heating. The more Fe_2O_3 was doped, the lower the f-CaO contents of samples. There are two explanations for Fe_2O_3-promoted microwave clinkering. On the one hand, three ratios (KH, SM, IM) of the samples with Fe_2O_3 all decreased (Table 2). As a result, the sintering kinetics of the samples was improved. On the other hand, the microwave absorption of ferric oxide was very strong in the sintering range. This caused the temperature of the burned materials to increase drastically. It was found that when the samples with Fe_2O_3 were heated for about 10 s in the microwave cavity, the light was seen and the materials sintered quickly. As for the two effects of Fe_2O_3 on material sintering, we believe that the latter was principal. For example, the quantity of Fe_2O_3 in Samples #2 was only 1%. When compared with Samples #1, their three ratios decreased a little, but their f-CaO contents decreased greatly. On the other hand, the quantity of Fe_2O_3 in the Samples #4 was 3%. Their three ratios decreased a lot compared with Samples #1 and #2, but their f-CaO contents were close to those of Samples #2. According to the experiment results, Samples #1, in which Fe_2O_3 was not doped, did not have strong microwave absorption until they were heated to 1300 °C in the electric furnace. Samples #2 and #4, in which Fe_2O_3 were doped, had strong microwave absorption when heated in electric furnace at about 1000 °C. Then why was the microwave absorption ability of Samples #1, in which no Fe_2O_3 was doped, but in whose chemical compositions on ignited basis Fe_2O_3 occupied 4.52%, so different from that of Samples #2? Is it because there exists a critical value with regard to the quantity of Fe_2O_3? Or is it because the microwave absorption of the iron compounds in the raw meal (industry raw material and its iron correcting material was slag of smelting copper) was low? This is a new problem that needs to be studied.

Table 3
The f-CaO contents of the sintered materials (%)

	Electric heating temperature (°C)	1000	1100	1200	1300	1300	Room temperature
No.	Microwave heating time (s)	135	90	60	40	(1 h soak)	25 min
1	Powder	4.25	3.32[a]	4.86[b]	0.97[c]		Loss 34.28%
	Piece	6.10	5.20	4.28[b]	2.97[c]	5.57	
2	Powder	2.27	1.37	1.68	0.65		Loss 33.48%
	Piece	0.91	1.54	2.73	1.55		
3	Powder	1.95	1.30	1.68	1.03		
4	Powder	1.63	0.85	1.04	0.91		

Powdered specimens #1 and #2 were only heated for 25 min with microwave, and their losses were 33.48% and 32.88%, respectively. Accordingly, $CaCO_3$ was not yet decomposed. So their f-CaO contents were not determined.

[a] Microwave heating time of the sample was 105 s.

[b] Microwave heating time of the sample was 95 s.

[c] Microwave heating time of the sample was 70 s.

The f-CaO contents of piece samples were more than those of corresponding powdered samples except for very few data. It seemed that the sintering tendency of piece samples was worse than that of powdered samples.

From the XRD pattern of each group, it could be noticed that the main minerals composition of the samples included C_3S, β-C_2S and ferrite solid solution. The diffractional peaks of C_3A and CaO were clear in the XRD pattern of Sample #1. There was no difference between the mineral compositions of the samples used in the experiments of microwave-promoted burning and electric heating. The characteristic XRD peaks of all the minerals were similar, too. XRD patterns showed that Portland cement clinkers were indeed formed after the burning was promoted with microwave heating for 40–135 s.

Figs. 2 and 3 show most of the alite crystals exhibit the ‘‘normal’’ sheets form generally observed in industrial clinkers. The belite appear less and distribute among the alite. The crystal size and distribution are different with the burning technology.

5. Conclusions

1. Compared with conventional electric heating, the new method of combining conventional electric heating with microwave heating is more efficient, and the speed of mineral formation is also faster. After being heated to a low electric heating temperature (1000–1100 °C) and then promoted with microwave burning in 1–2 min, Portland cement clinkers could be formed.

2. The mineral composition of Portland cement clinkers with this method is similar to that of the clinkers with conventional method. Their XRD peaks of minerals are similar too.

3. When Fe_2O_3 was mixed, the microwave absorption ability of the raw meals can be increased, and the burning temperature and microwave heating time can be decreased.

4. It seems that powdered samples are easier to burn than piece samples when the combined heating method is adopted.

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