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Solid-phase Decarburization Kinetics of High-carbon Ferromanganese Powders by Microwave Heating

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Abstract: Solid-phase decarburization of high-carbon ferromanganese powders (HCFPs) was conducted using calcium carbonate powders (CCPs) as a decarburizer by microwave heating. Solid-phase decarburization kinetics was investigated by isothermal method. The results show that the HCFPs show excellent microwave absorption at a higher average heating rate of 80 °C/min, while CCPs exhibit poor microwave absorption at a lower heating rate of 5—20 °C/min; the heating characteristics are in-between when HCFPs and CCPs are mixed. The average heating rates of the mixture are 32. 14, 31. 25, 31. 43, and 30. 77 °C/min when the mixture is heated up to 900, 1000, 1100, and 1200 °C, respectively. The good microwave absorption property of the mixed material lays the foundation for the solid-phase decarburization of HCFPs containing CCPs is a first-order reaction by microwave heating. Apparent activation energy of solid-phase decarburization is 55.07 kJ/mol, which is far less than that of ordinary carbon gasification reaction and that of solid-phase decarburization under the same decarburization condition by conventional heating. It indicates that microwave heating not only produces thermal effect, but also has non-thermal effect.

Key words: high-carbon ferromanganese powder; solid-phase decarburization; kinetics; microwave heating; calcium carbonate powder

With the rapid development of the low carbon alloy steel such as Cr-Mn stainless steel^[1-3], the decarburization of ferromanganese has attracted special attentions in the metallurgical field^[4-5]. Because of the relatively high vapor pressure of manganese and great binding energy between manganese and oxygen, the decarburization of ferromanganese in liquid phase is hard to occur^[6].

Compared with liquid-phase decarburization, solid-phase decarburization can reduce evaporation intensity of manganese and improve the recovery of manganese, so in the recent years, it has become a hot research topic. However, solid-phase decarburization relies on diffusion contact among carbon atoms at the reaction interface, with nucleation and phase formation during the process. Therefore, solid-phase decarburization requires a longer reaction time and higher reaction energy than liquid-phase decarburization does^[7]. Thus, it is a significant concern.

American scholars^[8] investigated the decarburization of ferromanganese by SiO₂ in vacuum, but the sample was easy to be contaminated by unreduced SiO₂, and gas products generated were detrimental to vacuum. Yan et al. ^[9] studied the solid-phase decarburization of high-carbon ferromanganese (HCF) with manganese oxide in vacuum. However, unroasted high-carbon ferromanganese powders (HCFPs) were mixed with manganese oxides generated by oxidizing roasting of HCFPs, and then they were decarburized in vacuum. The process flow was more complex. Bhonde and Angal^[8] used CO₂ as the decarburizer in his decarburization research on HCF, but it needs a long decarburization time at a decarburization ratio of 50. 73%.

Microwave heating technology offers the characteristics of rapid body heating as a new green metallurgy method and is suitable for metallurgical powder materials^[10]. Materials can be quickly heated

by microwave in a non-contact closed system, without extraneous contamination. Microwave heating can enhance ion diffusion in solid-phase reaction^[11] and increase the solid-phase reaction rate^[12]. Highcarbon ferromanganese is easily made into powder and exhibits better microwave heating characteristics. Carbon diffusion is the rate-limiting step in the solid-phase decarburization of HCFPs. Thus, in microwave heating field, carbon diffusion of solidphase decarburization of HCFPs can be enhanced and solid-phase decarburization rate can be improved. Guo et al. [13] conducted a comparison of decarburization of HCFPs by conventional and microwave heating. The results showed that microwave heating had better decarburization effects than conventional heating. However, solid-phase decarburization kinetics of HCFPs was seldom reported.

In this study, taking calcium carbonate powders (CCPs) as a decarburizer, the solid-phase decarburization of HCFPs was conducted to investigate the kinetics of solid-phase decarburization.

1 Experimental Method

Lumpy high-carbon ferromanganese was hard and brittle. It was firstly made into coarse powder with size less than 0.3 mm using a ball mill, and then pulverized into fine powder with particles sizes less than 0.074 mm using a grinder. The chemical composition of HCFPs is shown in Table 1. The decarburizer used was industrial CCPs with particle sizes less than 45 μ m and chemical composition is shown in Table 2.

 Table 1
 Chemical composition of HCFPs
 mass %

 C
 Si
 S
 P
 Fe
 Mn

 6.61
 1.98
 0.058
 0.092
 16.32
 68.46

Table 2 Main chemical composition analysis of CCPs

					mass %	
$CaCO_3$	$MgCO_3$	SiO_2	$\operatorname{Al}_2\operatorname{O}_3$	Fe_2O_3	Others	Total
96.04	2.14	1.05	0.20	0.23	0.34	100

The ratio of carbon content of HCFPs and CO₂ content of CCPs is called as decarburization molar ratio. According to the decarburization molar ratio of 1:1, 641.5 g HCFPs and 358.5 g CCPs were weighed, mixed well and put into crucible made of light brick. Then, the crucible was placed into a self-designed microwave furnace. A 2.45 GHz mi-

crowave generated by a magnetron was introduced into a cavity. A K-type thermocouple (Ni-Cr and Ni-Si) shielded with a stainless pipe was used to measure the temperature at the center of the powder. The mixture of HCFPs and CCPs was heated up to 900, 1000, 1100 and 1200 °C, and decarburized at a holding time of 0, 20, 40, and 60 min respectively in the microwave heating field.

As a comparison experiment, HCFPs containing CCPs of the same ratios were decarburized under the same decarburization condition in a conventional muffle furnace.

The carbon contents of the decarburized samples were measured by an NXQ-2D carbon-sulfur analyzer.

2 Results and Discussion

2. 1 Characteristics of temperature rise of HCFPs and CCPs

Fig. 1 shows the characteristics of the temperature rise of HCFPs and CCPs by microwave heating. It can be seen that the HCFPs exhibit better microwave absorption at a rapid heating rate in the microwave field. Temperature rises to 800 °C within 10 min at an average heating rate of 80 °C/min. Then, the heating rate declines slightly and the heating curve tends to flatten. By contrast, CCPs have poor microwave absorption, and the heating rate of CCPs is relatively slow. The heating rate of CCPs is relatively fast in the former 20 min at an average heating rate of 20 °C/min, and then the heating rate slows down at an average heating rate of 5 °C/min. The metallic carbides are the good microwave absorption materials. And the main phases of HCFPs are the manganese-iron carbide phases. Thus, under the same experimental condition, HCFPs perform better in absorbing microwaves than CCPs do.

Thermogravimetric-differential thermal analysis was conducted for CCPs. The result is shown in Fig. 2.

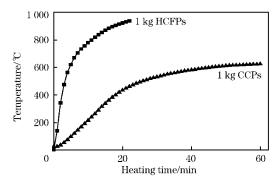


Fig. 1 Characteristics of temperature rise of HCFPs and CCPs by microwave heating

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