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LI LEI*,**, ZHANG LIBO*,***,****, DAI LINQING*,***,****#, ZHU HONGBO*,***,****,
CHEN GUO*,***,****, PENG JINHUI*,***,****, GUO QIN*,***,****

EFFECTS OF MICROWAVE SINTERING ON PROPERTIES AND MICROSTRUCTURE OF FERROMANGANESE ALLOY POWDERS

Microwave sintering process was employed to agglomerate ferromanganese alloy powders. The effects of sintering temperature, holding time and particle size composition on the properties and microstructure of sintering products were investigated. The results was shown that increasing sintering temperature or holding time appropriately is beneficial to increase the compressive strength and volume density. SEM and EDAX analysis shows that the liquid phase formed below the melting point in the sintering process, which leads to densification. XRD patterns indicate that the main reaction during microwave sintering is the decarbonization and carburization of iron carbide phase. The experiment demonstrate that the optimum microwave sintering process condition is 1150°C, 10 min and 50% content of the powders with the size of –75 μm.

Keywords: Microwave sintering; Ferromanganese powder; Densification; Liquid phase; Process conditions

1. Introduction

As an important alloy, ferromanganese is widely used as deoxidizer and desulfurizer for steelmaking. In addition, it is an essential alloying agent to improve the mechanical properties of steel such as hardness, ductility, toughness and anti-wear ability [1-3]. According to different carbon content of ferromanganese, it is divided into high carbon ferromanganese ($2.5\% < [C] \leq 7.0\%$), medium-carbon ferromanganese ($0.5\% < [C] \leq 2.5\%$) and low-carbon ferromanganese ($[C] \leq 0.5\%$) [4]. At present, Chinese ferromanganese alloy output is 10 million tons a year [5]. In the process of pouring, crushing, screening and transportation, about 8~10% powders of the ferromanganese will be generated [6]. Due to the large melting loss, the price of ferromanganese alloy powders is far lower than ferromanganese alloy block. Therefore, ferromanganese alloy powder is usually used as the raw material back to the electric arc furnace. This method not only influences production processes, but also reduces economic profits of ferroalloy enterprise. Melting ferromanganese alloy powders in conventional furnaces such as cupola furnace and induction furnace is another way, but there are possibilities of material and energy losses and some safety risks [7]. So the efficient usage of ferromanganese alloy powders is important and necessary.

Microwave energy is a form of electromagnetic energy with the frequency range of 300 MHz to 300 GHz [8]. Since the first report on microwave rapid heating particulate metals in 1999 by Roy et al. [9], the use of microwaves to consolidate a range of particulate metals and alloys has gained growing attentions during the past decade. A lot of researches have been performed in microwave sintering ceramics, ferrites and hard metals [10-12]. Comparing with conventional sintering, microwave sintering have many advantages such as faster heating rate, lower sintering temperature, enhanced densification, and save energy [13-15]. Therefore, consolidating ferromanganese alloy powders by microwave sintering is possible.

2. Experimental

The ferromanganese alloy powders used for the experiment was obtained from Dounan manganese industry Co., Ltd. Yunnan province, China. The chemical analysis of the ferromanganese alloy powders was shown in Table 1. The particle size distribution and the SEM image of the material were presented in Fig. 1 and Fig. 2, respectively. We can see that the powders are irregular and angular and the particle size larger than 150 μm accounts for nearly 52 percent of the material.

The ferromanganese alloy powders were sieved into different particle size fractions for future study. The samples were sintered in a microwave furnace in argon atmosphere. Microwave was generated by two magnetrons, which are operated at a frequency of 2.45 GHz, with power output in the range of

* NATIONAL LOCAL JOINT LABORATORY OF ENGINEERING APPLICATION OF MICROWAVE ENERGY AND EQUIPMENT TECHNOLOGY, KUNMING YUNNAN, 650093, PR CHINA.
** JIANGSU ENGINEERING CONSULTING CENTER, NANJING JIANGSU, 210003, P.R. CHINA.
*** STATE KEY LABORATORY OF COMPLEX NONFERROUS METAL RESOURCES CLEAN UTILIZATION, KUNMING UNIVERSITY OF SCIENCE AND TECHNOLOGY, KUNMING UNIVERSITY OF SCIENCE AND TECHNOLOGY, KUNMING YUNNAN, 650093, PR CHINA.
**** FACULTY OF METALLURGICAL AND ENERGY ENGINEERING, KUNMING UNIVERSITY OF SCIENCE AND TECHNOLOGY, KUNMING YUNNAN, 650093, PR CHINA.
\# Corresponding author: 372368763@qq. com

TABLE 1

Chemical composition of ferromanganese alloy powder

Component	Mn	Fe	C	Si	P	S
Wt.%	76.47	15.53	6.40	1.41	0.17	0.02

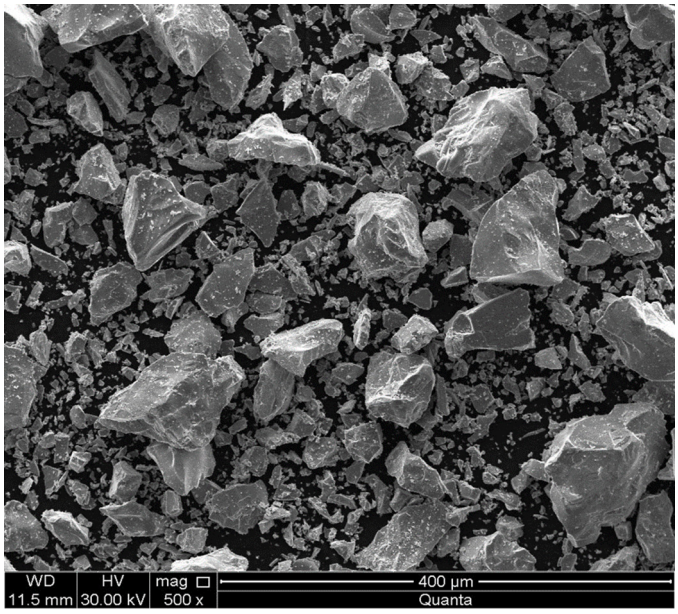

Fig. 1. SEM image of the material

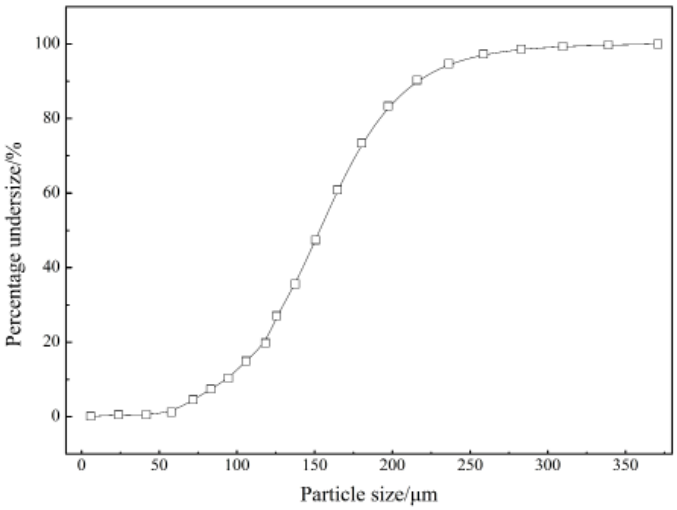

Fig. 2. Particle size distribution of the material

0~3 kW, in both single-mode and multi-mode operation. Temperature was measured using a thermometer with shielding pipe. Fig. 3 displays the schematic of the microwave furnace for this work. When sintering process was completed and the sample was cooled in oxygen free atmosphere to room temperature after turning off the microwave. All the sintered samples were cut into cubes with the length of 10 mm by wire-electrode. The solid densimeter (EDS-300, China) and mechanics experimental machine (AG-X-100KN, Japan) were used to test volume density and compressive strength of the samples. The microstructures of the sintered samples were observed under a scanning electron microscope (XL30ESEM-TMP, Philips, Holland) and the EDAX attached to the SEM was used for semi-quantitative chemical analysis. The crystal structure of the ferromanganese alloy powders and sintered samples were measured using XRD (D/Max 2200, Rigaku, Japan).

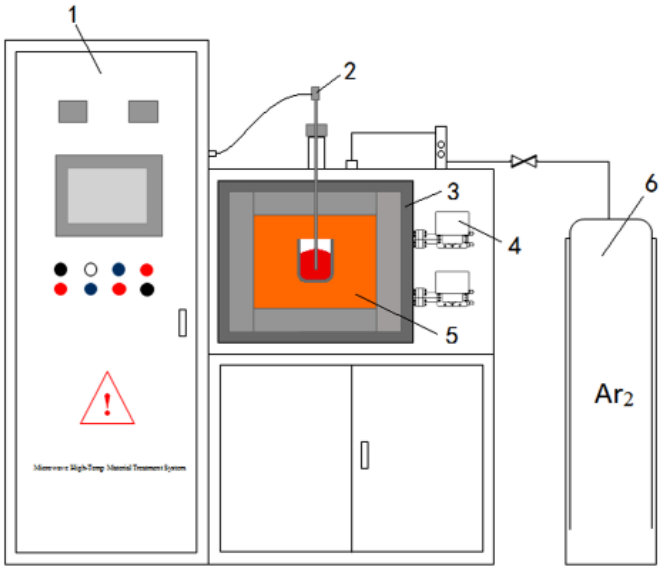

Fig. 3. Schematic diagram of microwave sintering device (1 – Control system; 2 – Thermocouple; 3 – Multimode cavity; 4 – Magnetron; 5 – Al_2O_3 fibre; 6 – Gas cylinder)

3. Results and discussion

3.1. Microwave heating characteristic

The microwave heating curves of different particle size materials with the weight of 250 g and microwave power of 1.5 kW were investigated. The results were illustrated in Fig. 4. The ferromanganese alloy powders was rapidly heated by microwave and the heating rate of early period was faster than that of latter. The particle size has a significant impact on heating rate. The powders with grain size larger than 270 µm heated to 1200°C from room temperature takes about 39 minutes, but the powders with grain size less than 75 µm just need 23 minutes with the average heating rate of 52°C/min. Decrease of grain size is beneficial to shorten the total microwave sintering process time.

Microwave heating in metals is different from dielectric materials. The bulk metals reflect microwaves because no internal electrical field is induced in it. Microwave interaction with metals is only restricted to its surface. This depth is also called as skin-depth (δ), which is defined as the distance into the metal at which the incident power drops to $1/e$ of the surface value. The skin depth is mathematically expressed as follows [16]:

$$\delta = \frac{1}{\sqrt{\pi f \sigma \mu}} \tag{1}$$

Where f is microwave frequency. μ is magnetic permeability. σ is electrical conductivity. Therefore, δ values of different ferromanganese alloy powder are the same under a certain temperature in this experiment.

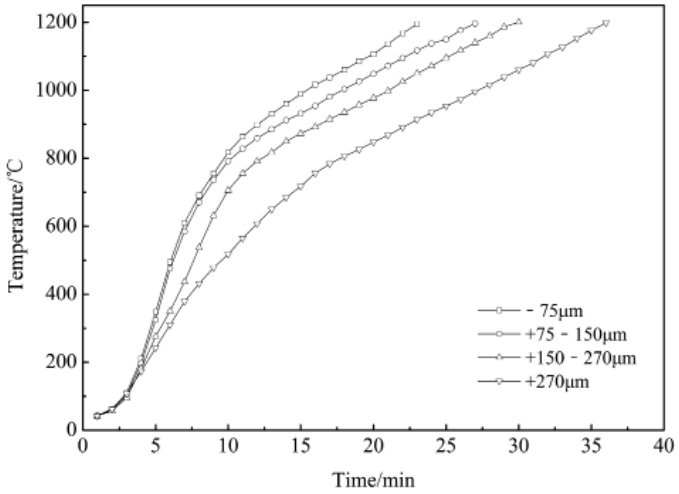

Fig. 4. Temperature characteristic of different particle size materials by microwave heating

Fig. 5 shows the simplified model of alloy powder heated by microwave. We assume that the alloy powder is spherical. R is the radius of the alloy powder and r is the radius of the unheated part, $r = R - \delta$. The volume ratio (η) of heated part and alloy powder is expressed as follows:

$$\eta = 1 - \left(1 - \frac{\delta}{R}\right)^3 \tag{2}$$

A higher value of η indicates a higher microwave heating efficiency [11]. η decreases with R increase, so the ferromanganese alloy powders with smaller size is more easily to be heated by microwave.

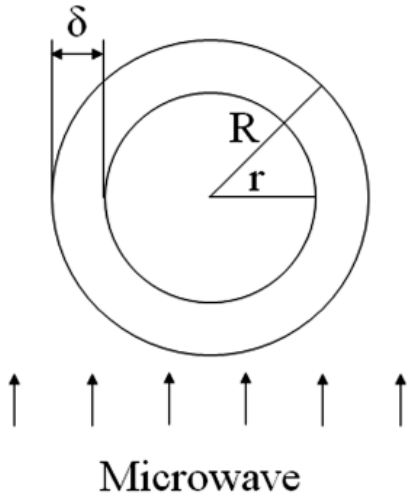

Fig. 5. The model of alloy powder heated by microwave

3.2. Ferromanganese agglomerates properties

Fig. 6 shows the compressive strength and volume density of agglomerates sintered at different process conditions. Testing result shows that the compressive strength of ferromanganese alloy from the manufacturer, the volume density and the melting point are 340 MPa, 6.8 g·cm^{-3} and 1260°C, respectively.

The particle size of the sample is –75 μm, which was sintered at different temperatures for 10 minutes hold and the influences of sintering temperature are illustrated in Fig. 6 (a). It is obvious that with the increase of sintering temperature from 950°C to 1200°C, the compressive strength and volume density were increased. The values of compressive strength and volume density at 1150°C were significantly larger than that at 1100°C, which reached about 387 MPa and 5.85g·cm^{-3}, respectively. The compressive strength of ferromanganese agglomerates is greater than ferromanganese alloy

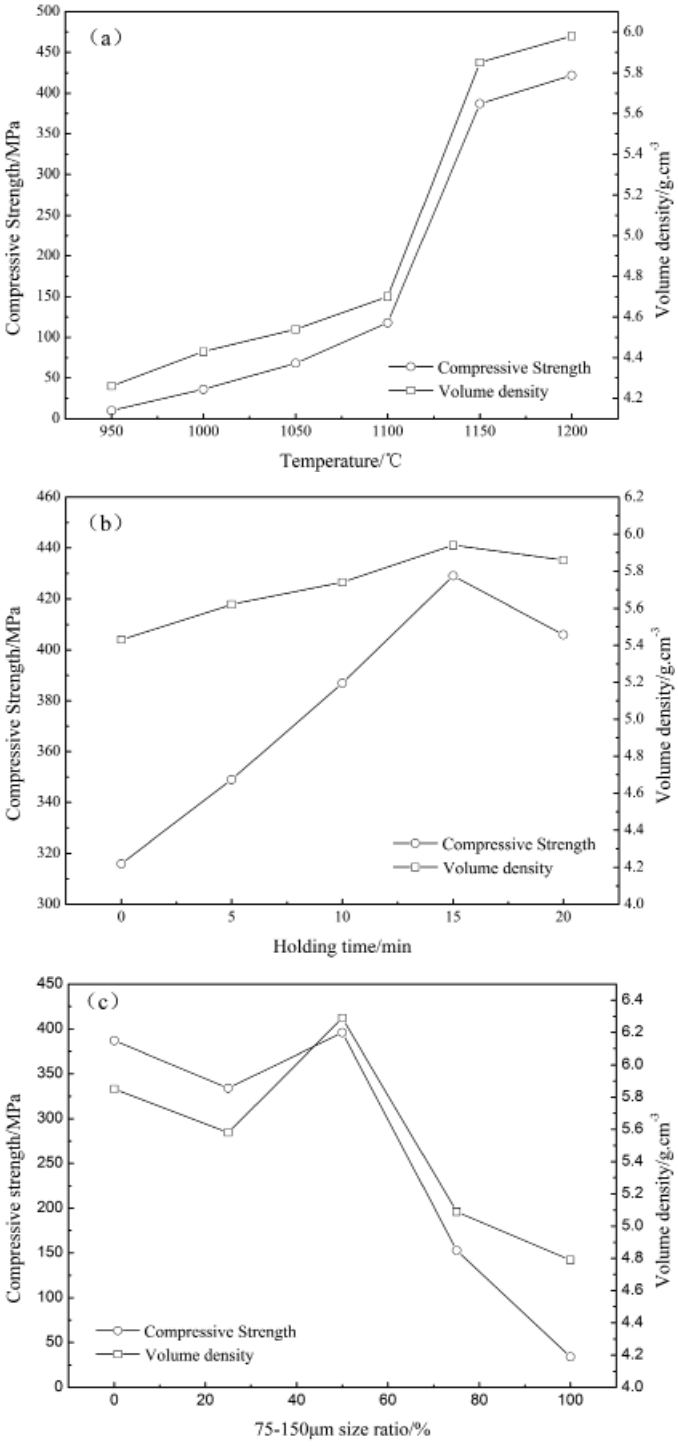

Fig. 6. Effects of (a) sintering temperature, (b) holding time and (c) 75-150 μm size ratio on properties of ferromanganese agglomerates

The influences of holding time was also investigated at sintering temperature of 1150°C. As can be seen from Fig. 6 (b) that the compressive strength and volume density increased firstly and then decreased with increase the holding time. The maximum values occurred at 15 minutes are 429 MPa and 5.94 $g \cdot cm^{-3}$, respectively. Considering the demands of energy saving and compressive strength, 10 minutes is reasonable.

Ferromanganese alloy powders with the size of –75 μm has good microwave heating characteristic, but we need consider the difficulties of ball-mill process before sintering in industrialized production. In order to reduce the use of –75 μm powders, the –75 μm and +75–150 μm ferromanganese alloy powders were mixed up according to a certain ratio. Then, they were sintered at 1150°C for 10 minutes hold. The effects of the content of +75–150 μm powders on compressive strength and volume density are shown in Fig. 6 (c). The compressive strength and volume density value of sintered sample with 25% content of +75–150 μm powders was less than that of the sample sintered by 100% content of –75 μm powders. When the content of +75–150 μm size powders is 50%, the compressive strength and volume density of the sintered sample were increased to maximum value of 396 MPa and 6.29 $g \cdot cm^{-3}$, respectively. With the increase of the content of +75–150 μm powders from 50% to 100%, the compressive strength and volume density value rapidly decreased which was lower than ferromanganese alloy.

3.3. Microstructure analysis

Fig. 7 shows the typical microscopy images of ferromanganese agglomerates under different microwave sintering conditions. Fig. 7 (a) was sintered at 950°C for 10 minutes and all the particle size of the powders was less than 75 μm. As can be seen, the particle size shape and appearance of powders show little changes and the phenomena of agglomeration is not obvious. Fig. 7 (b) was sintered at 1100°C. It's clear that parts of powders have stuck together but they have not formed a block. A large number of irregular pores exist in ferromanganese agglomerate. Fig. 7 (c) was sintered at 1150°C and the holding time was 0 min. Comparing with Fig. 7 (b), the powders have become a block and the pores have been spheroid. When holding time extended to 15 minutes, as Fig. 7 (d) shows, the pores saw in micrographs are relatively smaller and more rounded. Fig. 7 (e) was sintered at 1150°C for 10 minutes and the particle size of the powders was large than 75 μm and less than 150 μm. We can observe that the particle edges stuck together and large area of space were exist among the particles. In Fig. 7 (f), the content of +75–150 μm size powders and –75 μm size powders was 50% and 50%, respectively. The microstructure of agglomerate seems similar to the alloy block. There is no obviously pores in it but have a little small cracks. Fig. 7 indicated that the relative density of ferromanganese agglomerates increased with the increase of sintering temperature or holding time. The ratio of +75–150 μm size powders and –75 μm size is the key factor to rapid densification method.

Fig. 8 shows typical SEM micrographs and EDAX of microwave sintering samples in different temperature. It can be observed from Fig. 8 (a) that small-sized alloy powders and the particle surface melt into liquid, at first, although the sintering temperature was much lower than melting point, which may be caused by hot spots. Due to lower sintering temperature, the volume of the appeared fluid is relatively small. Raising the temperature to 1150°C, as Fig. 8 (b) shows, large amount of liquid phase generated. The extinction of liquid phase accelerates the re-arrangement of the grains and enhances the densification by filling the clearance between solid grains. So the volume density and compressive strength of the ferromanganese agglomerate increased, when temperature was 1150°C. In sintering process, densification is fast and the porosity decreases with the increase of the holding time. The microwave become harder to penetrate because of densification, so microwave heating rate of later period decreased and too much holding time almost had no effect on improve the properties of ferromanganese agglomerate. Upon stopping heating, the sample cooled and liquid phase binded unmelted powders to achieve agglomeration. Fig. 8 (c, d) shows peaks of carbon, manganese and iron elements observed from the EDAX analysis. It is evident that there is no oxygen reaction with the samples during the sintering process.

3.4. Phase and chemical composition

The crystalline structures of ferromanganese powders before and after microwave sintering are characterized by X-ray diffractometer at a scanning rate of 0.25°/min with 2θ ranging from 30° to 72.5°. After scanning, the mineral peaks of the samples are identified. The XRD patterns of the manganese ore and the microwave heated products are shown in Fig. 9. It can be seen from Fig. 9 that the main phase of raw materials are Mn_5C_2 (JCPDS card No. 80-1700) and Fe_7C_3 (JCPDS card No. 17-0333). Comparing with raw materials, the phase of iron carbide at 1100°C and 1150°C changed into Fe_3C (JCPDS card No. 85-1317) and Fe_5C_2 (JCPDS card No. 51-0997), respectively. The sintered product at 1200°C with the same composition as the raw material, but the peak intensity of Mn_5C_2 and Fe_7C_3 decreased. The results of XRD analysis indicate the reaction of iron carbide phase may be expressed as follows:

$$3Fe_7C_3 = 7Fe_3C + 2C$$

$$5Fe_3C + C = 3Fe_5C_2$$

$$7Fe_5C_2 + C = 5Fe_7C_3$$

Besides the compressive strength and volume density properties of agglomerates, the chemical composition of sintering products is also important, because it is directly related to the level of product prices. Table 2 shows the chemical composition of ferromanganese agglomerates in different sintering process conditions. It can be found from Table 2 that the manganese content decreased with the increase of temperature and holding time because of the volatilization loss in high temperature. So

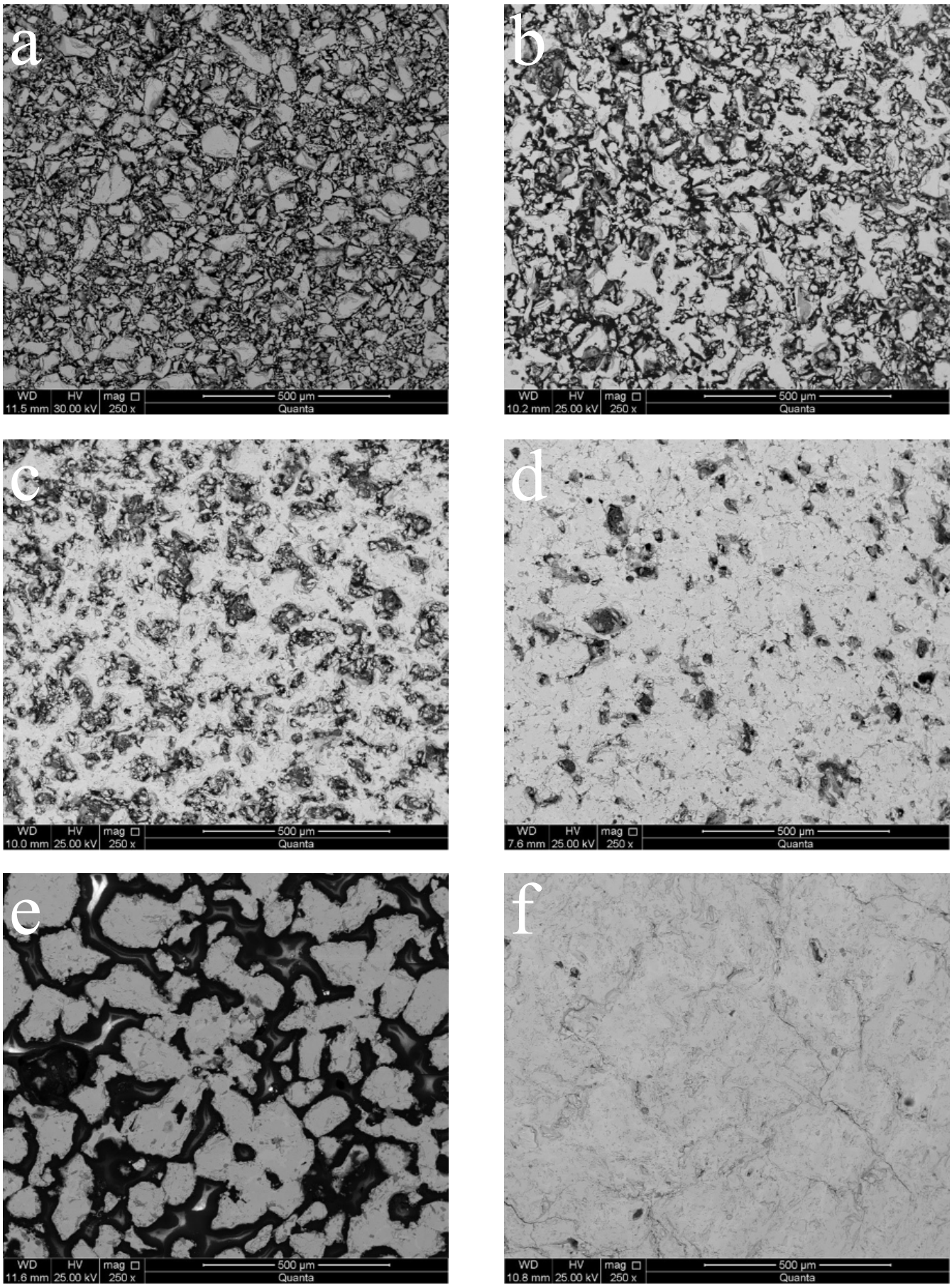

Fig. 7. Microstructures of ferromanganese agglomerates sintered at different process conditions, (a) 950°C, 100% of –75 µm,10 min; (b) 1100°C, 100% of 75 µm, 10 min; (c) 1150°C,100% of –75 µm, 0 min; (d) 1150°C, 100% of –75 µm, 15 min; (e) 1150°C, 100% of +75–150 µm, 10 min; (f) 1150°C, 50% of +75–150 µm, 10 min

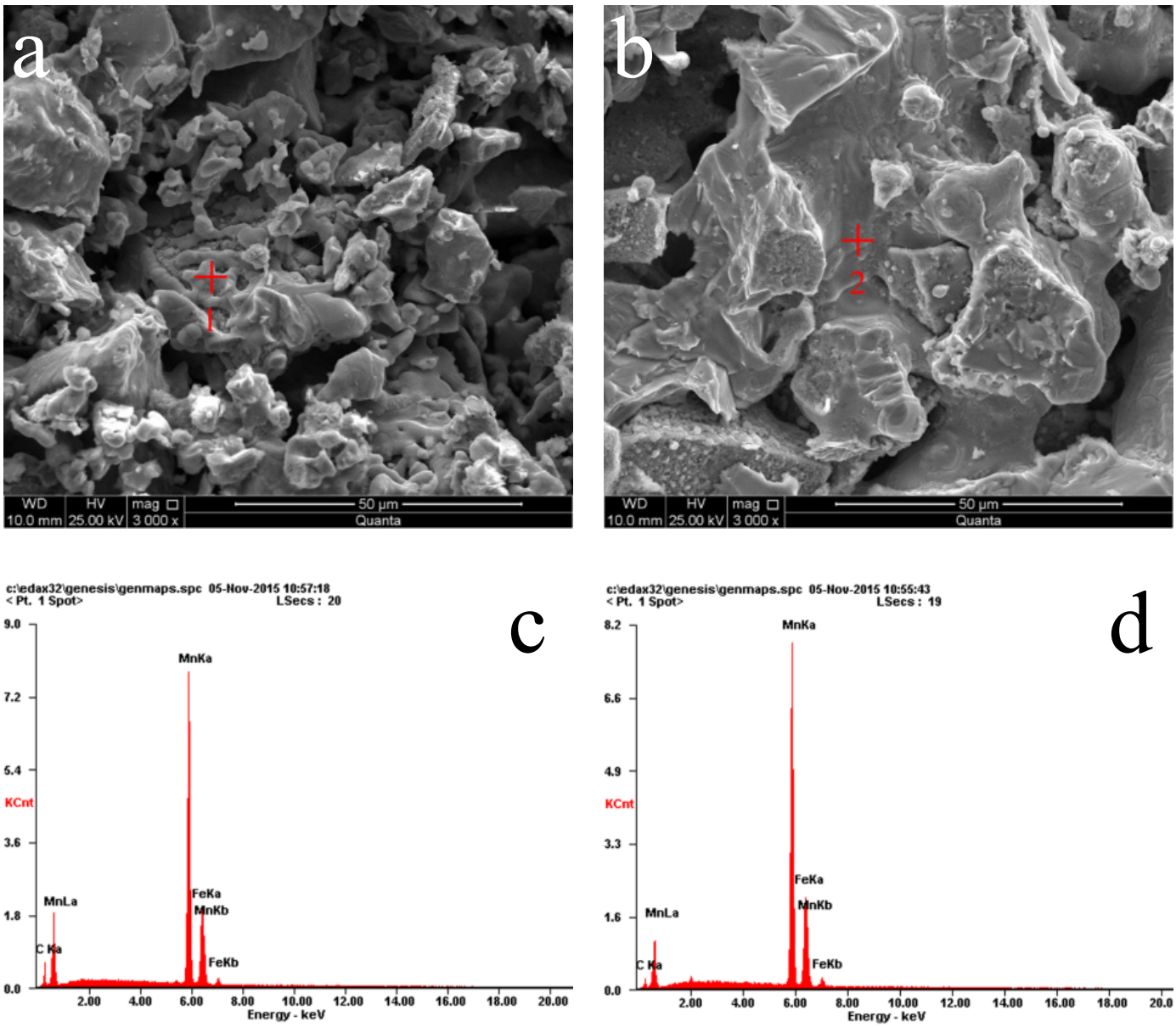

Fig. 8. SEM images and EDAX of liquid phase in different sintering temperature, (a) 1050°C, 0 min; (b) 1150°C, 0 min; (c) EDAX of spot 1; (d) EDAX of spot 2

it is not necessary to set too high sintering temperature and too long holding time under enough compressive strength premise. The chemical composition of sintering product with 50% content of –75 µm size ferromanganese powders is similar to raw materials and the chemical composition can meet standard of FeMn78C8.0 (GB/T 3795-1996, China).

TABLE 2

Chemical composition of ferromanganese agglomerates

Microwave Sintering Process			Element					
Temperature (°C)	Time (min)	–75 µm Content (%)	Mn	Fe	C	Si	P	S
1100	10	100	76.21	15.34	6.56	1.36	0.16	0.019
1150	10	100	75.37	16.09	6.48	1.41	0.15	0.014
1150	10	50	76.09	15.79	6.34	1.34	0.16	0.016
1150	20	100	74.93	16.54	6.58	1.61	0.15	0.019
1200	10	100	73.04	17.11	6.91	1.76	0.20	0.023

4. Conclusion

In this research, the sintering process of ferromanganese alloy powders using microwave heating was systematically investigated. Microwave heating curve indicated that the smaller the alloy powders particle was, the more faster heating rate was. –75 µm size powders were heated to 1200°C which need only 23 minutes. The compressive strength and volume density of ferromanganese agglomerates is closely related to sintering temperature, holding time and particle size composition. At the microwave sintering temperature of 1150°C, holding time of

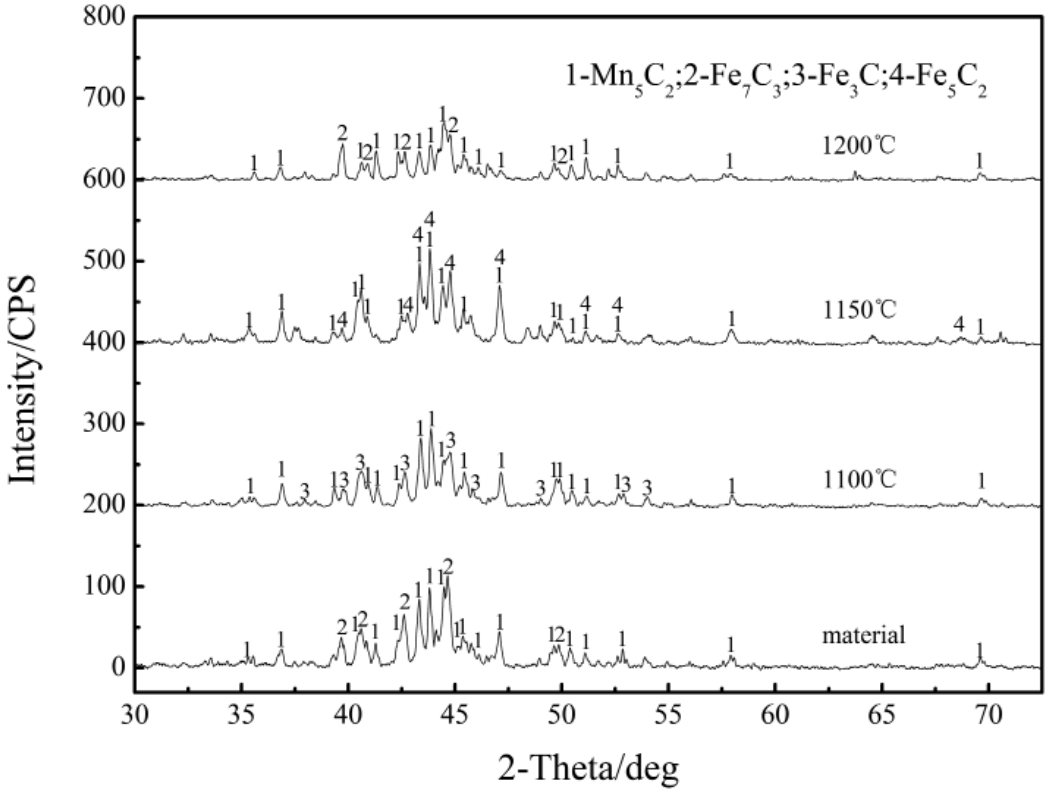

Fig. 9. XRD patterns of raw materials and microwave sintering products

10 min and +75–150 μm powders content of 50%, the value of compressive strength and volume density of the sintered sample are 396 MPa and 6.29 g · cm^{-3}, respectively. At the same time, the chemical composition can meet the standard of FeMn78C8.0. The ratio of +75–150 μm size powders and –75 μm size powders is the key factor of microwave sintering ferromanganese alloy powders. XRD analysis indicates that the main phase of raw materials are Mn_5C_2 and Fe_7C_3. During microwave sintering process, Fe_7C_3 transforms into Fe_3C or Fe_5C_2. SEM images show that the small-sized alloy powders and the particle surface melt into liquid first, then pores is tightened and spherized. This study suggests that microwave sintering is feasible, economic and efficient.

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