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Influence of microwave treatment on grinding and dissociation characteristics of vanadium titano-magnetite

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Abstract: The effect of microwave treatment on the grinding and dissociation characteristics of vanadium titano-magnetite (VTM) ore were investigated using scanning electron microscopy (SEM), nitrogen absorption measurements, particle size distribution measurements, X-ray diffraction (XRD) analysis, Fourier transform infrared (FT-IR) spectroscopic analysis, and magnetic separation. SEM analysis showed that microfractures appeared in the microwave-treated VTM, which is attributed to the microwaves' selective heating characteristic and the differential expansion between minerals and gangues. Nitrogen absorption showed that the microfractures were more pronounced when the microwave heating time was increased. Particle size distribution analysis showed that microwave treatment could improve the grindability of the VTM, thus increasing the weight percent of the fine-ground product. The increase in grindability was more significant with prolonged heating time. Moreover, the particle size distribution of the fine-ground product changed only slightly after the microwave treatment. XRD analysis showed that the crystallinity of the microwave-treated VTM increased with increasing microwave heating time. The magnetic separation tests revealed that the separation efficiency increased as a result of the intergranular fractures generated by microwave treatment. The Fe grade of the magnetic fraction of microwave-treated VTM was 1.72% higher than that of the raw ore. We concluded that the microwave treatment was beneficial, especially for the mineral processing characteristics.

Keywords: microwave treatment; vanadium titano-magnetite; grinding; microstructure; magnetic separation

1. Introduction

Thermally assisted dissociation has been widely used as a method to decrease ore hardness before beneficiation and to improve the degree of liberation by generating thermally induced fractures within ore particles [1–4]. Microwave heating has many advantages over conventional heating, including flash heat, effective power consumption, quick starting and stopping, and less environmental impact [5–7]. The dominant mechanism by which microfractures are generated is the faster microwave-induced heating of metal minerals in the interior of the ore particles compared with the heating of metal minerals on the exterior of the particles. Heat is produced by molecular tribology within the ore lattice of the minerals, which corresponds to electromagnetic field vibration, and is then transferred via thermal transmission into other surrounding minerals [8–11]. Numerous reports have demonstrated that microwave heating could feasibly increase ore grindability and enhance the liberation of metallic minerals [12–16].

Vanadium titano-magnetite (VTM) ore has a complex phase composition that includes the phases ilmenite, magnetite, and magnetic pyrite as well as other minerals [17]. Thus, the dissociation of VTM ore is more complex than that of other congeneric ores; it requires much more energy and more grinding cycles to achieve a relatively high mineral processing index. Therefore, the ore pretreatment process is critical for the grinding–magnetic separation processing of VTM. Investigations of the various properties of untreated and microwave-treated VTM provide guidance for making use of VTM ore.

In recent decades, numerous researchers have concentrated on the microwave pretreatment of ores. Zhong *et al.* [16] researched the degree of liberation of rare-earth ores pre-

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treated with microwaves and found that the microwave radiation could improve the degree of liberation of the ore. Kingman *et al.* [18] reported that microwave treatment affected the strength of lead–zinc ore; they found that the strength of ore could be decreased by 50% in 0.1 s at 15 kW of microwave power. Rizmanoski [8] investigated the influence of microwave treatment on the strike breakage of copper ore and concluded that ore heated at 5 kW for 5 s was frailer than the untreated ore. Furthermore, better liberation could be achieved using a higher microwave power level. The influence of microwave heating on the magnetic properties of pyrite has been investigated by Waters *et al.* [19]. They carried out comparative batch magnetic separation tests on ore treated at 1.9 kW for 120 s and found that the recovery rate in the magnetic concentrate increased from 8% in wet conditions and 25% in dry conditions to greater than approximately 80% for both processes. The increase in the recovery rate was ascribed to the microwave treatment changing the chemical properties of the ore.

The purpose of the present investigation is to characterize and analyze the microstructure and dissociation characteristics of VTM ore under different microwave heating times, using scanning electron microscopy (SEM), nitrogen absorption, particle size distribution, X-ray diffraction (XRD) and Fourier transform infrared (FT-IR) spectroscopy. A secondary objective is to compare the mineral processing properties of microwave-treated VTM with those of the initial VTM in magnetic separation processing.

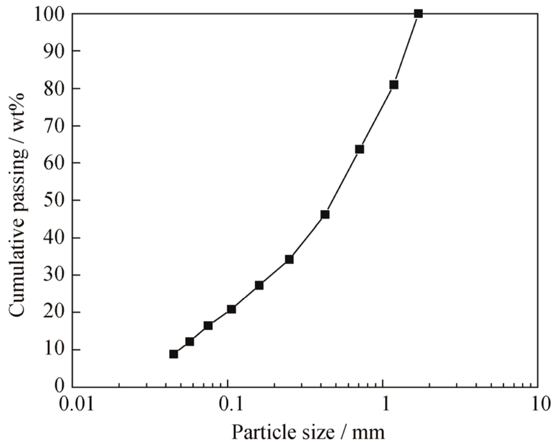

Fig. 1. Particle size distribution of the VTM (< 1.4 mm).

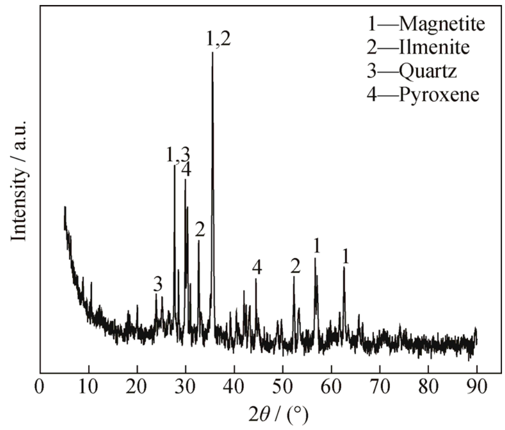

Fig. 2. X-ray diffraction pattern of the VTM.

Table 1. Main chemical composition of the VTM wt%

TFe	TiO_2	V_2O_5	SiO_2	MgO	CaO	Al_2O_3
28.55	9.86	0.23	29.52	11.85	7.36	8.78

2. Experimental

2.1. Materials

The samples were collected in Panzhihua, Sichuan province, China. VTM was first crushed to < 1.4 mm using a jaw breaker; this particle size was determined to be the ball mill feeding requirement. The particle size of the VTM is displayed in Fig. 1, which is mainly distributed in the range from 0.2 to 1.7 mm. The chemical composition of the VTM is shown in Table 1. Mineralogical analysis of the VTM was performed using X-ray diffraction (Fig. 2). Magnetite and ilmenite were the dominant mineral phases associated with quartz in the ore; pyroxene and other impurities were present as the gangues.

2.2. Experimental methods

2.2.1. Microwave treatment

Microwave treatment was performed in a microwave workstation (MobileLab, Tanshan Nayuan Instruments Ltd., China) with a continuous power-level range from 0 to 4 kW. The inner dimensions of the microwave cavity were 400 mm (length) × 400 mm (width) × 500 mm (height). The energy output of the microwave workstation was generated by four magnetrons (2.45-GHz frequency), each operated at 1 kW and each cooled by an air cycle. The temperature was measured using a K-type thermocouple, which was separated from the sample by a thin layer of carbon paper placed at the closest proximity to the irradiated sample in the oven. During the microwave heating experiments, 100 g of VTM was placed in the microwave oven and irradiated for different heating times at a power level of 4 kW. The treated ore was then naturally cooled within the oven to room temperature.

2.2.2. Grinding and magnetic separation tests

A conical ball mill (XMQ ϕ240 mm × 90 mm, Wuhan Exploring Machinery Plant, China) was used to grind the

VTM ore before and after the microwave treatment. During the grinding, VTM was equably placed in a 6.5-L conical ball mill with 11.09 kg of 8−10 mm steel balls; the mill was operated at 96 r/min. Five hundred grams of ore sample was used, each at a pulp density (mass/mass) of 65wt%. The weight percent of the fine-ground product under 0.074 mm was determined at different grinding times using a sieving analysis method.

The ground products (10 g) of untreated and microwave-treated VTM were subjected to low-intensity (wet) magnetic separation using an electromagnetic separator (XCGS ϕ50 mm, Magnetic tube, China) under magnetic fields of different intensities.

2.3. Characterization

The crystalline phases of the samples were characterized by XRD carried out on an X'PERT PRO MPD/PW3040 (PANalytical B.V. Corp., The Netherlands) equipped with a Cu K_α radiation source. Samples were scanned at 0.25°/min over the 2θ angle range from 5° to 90°. The microstructures of the samples were analyzed by SEM (JSM-7800F, JEOL Ltd., Japan). Energy-dispersive X-ray (EDX) measurements were performed to determine the elemental composition at the samples' surfaces. The specific surface area (SSA) and pore volume (PV) were determined by nitrogen adsorption experiments (N0VA1200e, Quantachrome, USA). A laser diffraction analyzer (BT-9300H, Dandong Bettersize Instruments Ltd., China) was used to analyze the particle size distribution of the fine-ground product. The surface functional groups were characterized by FT-IR spectroscopy (Nicolet-380, Thermo Corp., USA) carried out over the spectral range from 4000 to 400 cm^{-1}.

3. Results and discussion

3.1. Heating rate of the VTM using microwave radiation

Fig. 3 shows the temperature curve of the VTM under microwave heating. The temperature of the ores increases with the increasing microwave heating time. Fig. 3 shows that the temperature of the VTM was as high as 480°C after 100 s of microwave heating. This rapid heating is due to the high microwave absorption capability of magnetite and ilmenite within the VTM ore and to the highly efficient transformation of microwave energy to thermal energy within a relatively short time. However, when microwave heating time exceeded 140 s, a small part of the VTM was melted and gathered. Therefore, the maximum microwave heating time was 140 s in subsequent experiments.

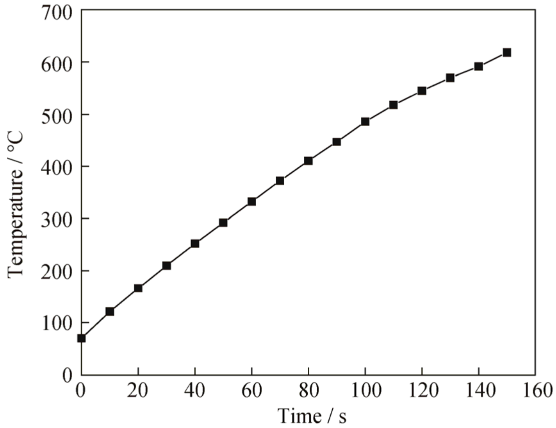

Fig. 3. Relationship between temperature and microwave heating time at 4 kW for the VTM.

3.2. SEM and nitrogen absorption analyses

The SEM analysis was carried out to give a better understanding of the influence of microwave treatment on the microstructure of VTM. The raw ore was characterized using SEM and EDX techniques, and the results are presented in Fig. 4. SEM analysis reveals that the surface of the raw ore has regular and tighter grain boundaries, and its structure is free of visible microfractures. EDX analysis of the different mineral surfaces of the raw ore show that the Fe and Ti contents were substantially higher in the valuable minerals than in the gangue minerals, whereas the Al, Mg, Ca, and Si contents exhibited the opposite trend.

Fig. 5 shows the section micrographs of VTM subjected to microwave heating for 140 s. Extensive microfractures occurred after microwave heating; some of the microfractures were transgranular, and some were along the grain boundaries (intergranular fractures). This fracture behavior is attributed to microwaves selectively heating the valuable minerals and to the differential expansion of valuable minerals and gangues. The characteristic of microwave heating results from the variable dielectric property of each mineral phase. The loss factor for gangues is quite low, whereas magnetite and ilmenite have relatively high loss factors [18]. This observation suggests that the metallic minerals in the ore exhibit faster heating under microwave irradiation than the rest of the gangues, which induces stress cracking in the ore particles. The microfractures in the ore particles were beneficial to increasing the grindability and dissociation of the microwave-treated VTM.

Table 2 shows that microwave treatment strongly influenced the SSA and PV of VTM. The SSA and PV of the microwave-treated VTM were higher than those of the raw ore because of thermally induced fractures. With increasing microwave heating time, the thermally induced stress increased, thus leading to serious damage to the microstructure of the microwave-treated VTM. Therefore, the SSA and PV of the VTM increased continuously, which means that the micro-fractures were more pronounced with increasing microwave heating time.

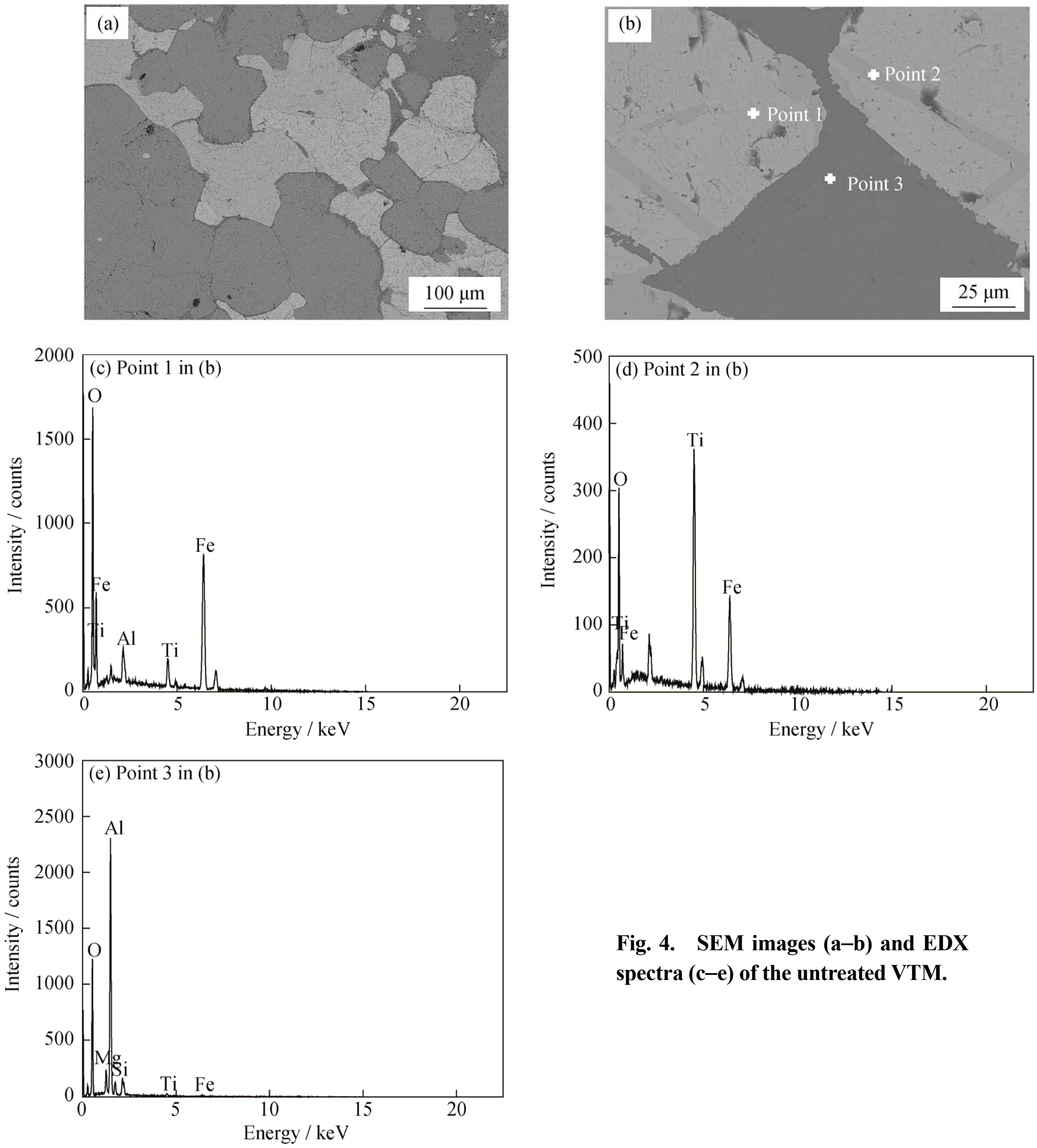

Fig. 4. SEM images (a–b) and EDX spectra (c–e) of the untreated VTM.

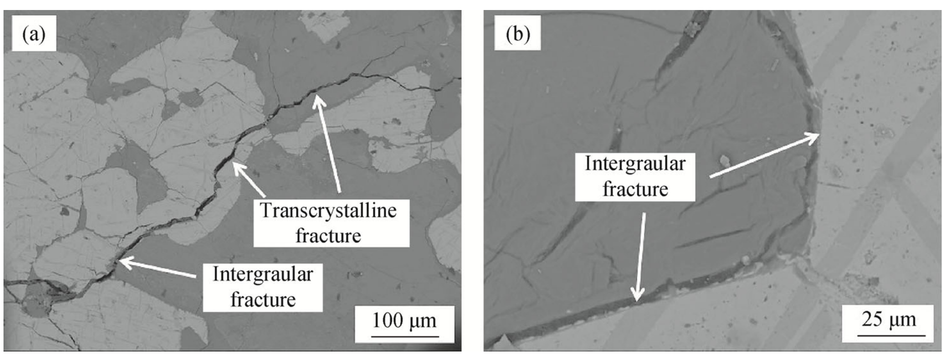

Fig. 5. SEM image of the microwave-treated VTM: (a) 200×; (b) 800×.

Table 2. Specific surface area and pore volume of untreated and microwave-treated VTM with 1.18–1.7 mm particle size

Microwave heating time / s	Specific surface area / ($m^2 \cdot g^{-1}$)	Pore volume / (10^{-3} $cm^3 \cdot g^{-1}$)
0	0.385	2.1245
60	0.401	2.8556
100	0.513	3.1566
140	0.553	3.5511

3.3. Particle size distribution analysis

VTM was ground for 4 min, and the particle size distribution of the ground product was determined by sieve analysis (Fig. 6). Fig. 6 shows that, with increasing microwave heating time, the influence of microwave heating on the output of the finer fraction increases. According to the previous analysis, with increasing microwave heating time, VTM assimilated more microwave energy and the temperature of the metallic minerals increased substantially, thus generating high thermal stress and resulting in serious destruction within the ore particle. Therefore, increasing the microwave heating time is reasonably concluded to positively affect the grindability of microwave-treated VTM.

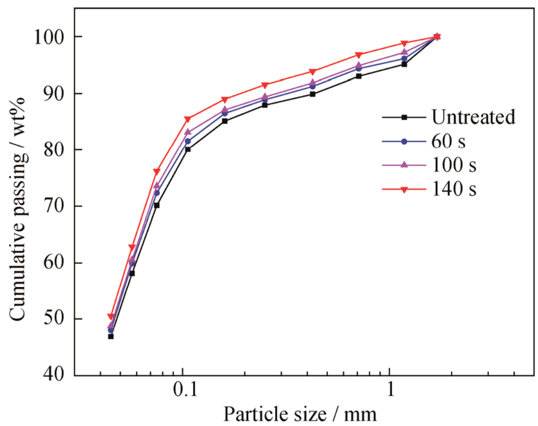

Fig. 6. Particle size distribution of the ground products of untreated and microwave-treated VTM ground for 4 min.

Both untreated and microwave-treated VTM were ground for various times, and the weight percent of ground product with < 0.074 mm particle size was determined. As evident in Fig. 7, the weight percent of the ground product with the < 0.074 mm particle size increased with increasing grinding time and microwave heating time. After a 4 min grinding period, the average weight percent of ground product with < 0.074 mm particle size was 45.48wt% in the untreated VTM. In the microwave-treated sample, the average weight percent of ground product with < 0.074 mm particle size increased to 47.43wt%, 49.23wt%, and 51.96wt% for samples irradiated for 60 s, 100 s, and 140 s, respectively. These results indicate that an appropriate extension of the microwave heating time would result in a higher weight percent of ground product with < 0.074 mm particle size. Therefore, microwave treatment can be used efficiently and effectively in the thermal treatment and grinding processing of VTM.

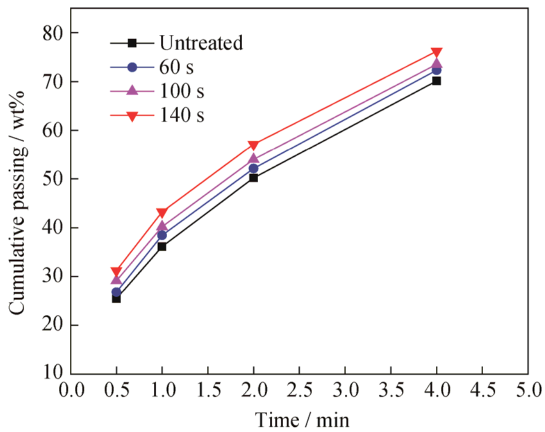

Fig. 7. Weight percent of ground product with < 0.074 mm particle size ground for different durations.

In general, the particle size of VTM ore should be controlled in a proper range in a magnetic separation process; that is, excessively fine particles might not contribute to an enhanced magnetic concentration index. The fine magnetic particles can cause magnetic reunion, which can lead to a low Fe grade of the concentrate. According to Fig. 8, the particle size distributions of the fine-ground products (< 0.074 mm particle size) changed only slightly after microwave treatment, which is a beneficial characteristic for the subsequent magnetic separation process.

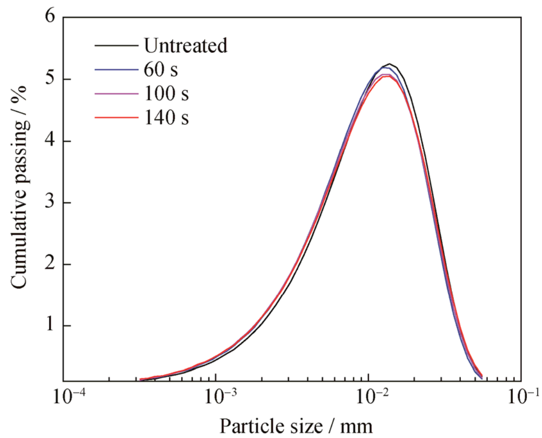

Fig. 8. Particle size distribution of fine-ground product (< 0.074 mm particle size) of untreated and microwave-treated VTM ground for 4 min.

3.4. XRD and FT-IR analyses

The XRD patterns of VTM before and after microwave heating for various times are provided in Fig. 9, where the pattern of the microwave-treated VTM specimen shows more pronounced peaks of phases than the pattern of the untreated VTM specimen. Regarding the microwave-treated VTM, the intensity of the peaks in its XRD pattern gradually increase with increasing microwave heating time. After 140 s of microwave treatment, the diffraction peaks of forsterite, kaersutite, and other impurity phases appeared. These results indicate that the crystallinity of the VTM ore increases with increasing microwave heating time. Similar findings have been reported by many other researchers [20–21]. The difference in the peak intensities might be due to the gangues being decomposed after microwave treatment, meanwhile, the combination of magnetite and ilmenite was separated.

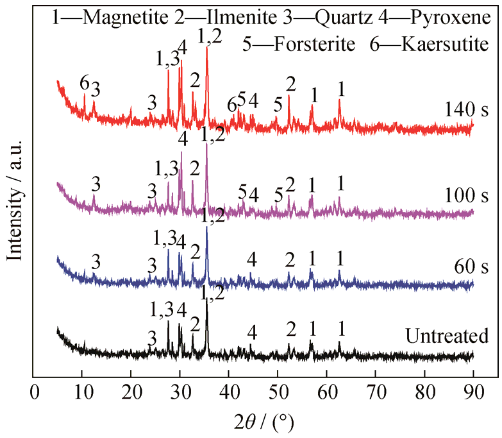

Fig. 9. XRD patterns of the VTM at different microwave heating times.

The FT-IR spectra of VTM treated for different microwave heating times were analyzed and compared (Fig. 10). The peaks at approximately 3433.8 cm^{-1} and 1637.6 cm^{-1} correspond to O–H stretching and O–H bending, respectively [22]. The two weak absorption bands at 1094.5 cm^{-1} and 1024.7 cm^{-1} were identified as the stretching vibrations of Si–O in $[SiO_4]$ tetrahedral units [23]. The absorption bands between 550 and 400 cm^{-1} were assigned to the stretching vibrations of metallic ions in the octahedral units. The changes in the FT-IR spectra after microwave treatment are consistent with the changes observed in the corresponding XRD patterns. The characteristic peaks of O–H groups gradually decreased in intensity with increasing microwave heating time as a consequence of dehydroxylation during the microwave treatment. Furthermore, the metallic ions and Si–O vibration bands increased in intensity. On the basis of the XRD and FT-IR analyses, we concluded that the VTM can be dissociated into valuable minerals and more gangues by microwave irradiation.

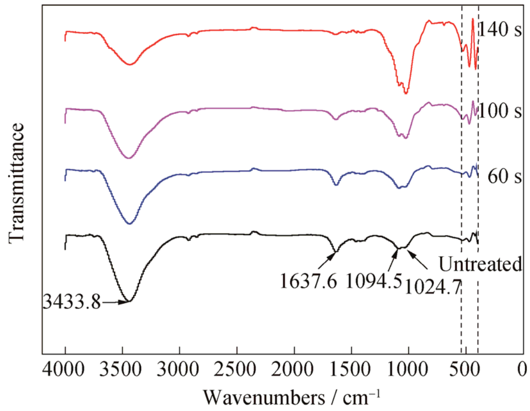

Fig. 10. FT-IR spectra of the VTM subjected to microwave heating for various times.

3.5. Magnetic separation analysis

Fig. 11 shows the Fe grade and recovery rate of the magnetic fraction of untreated and microwave-treated VTM ground for 2 min and subjected to magnetic fields of various intensities. The Fe grade of the magnetic fraction of microwave-treated VTM is higher than that of the untreated VTM under various magnetic field intensities. The discrepancies vary from 0.93% to 2.42%, with an average value of 1.72%. The recovery rate of the magnetic fraction of untreated and microwave-treated VTM changed slightly, which means that greater separation efficiency could be achieved by microwave pretreatment. The higher separation efficiency could be due to the greater degree of dissociation of the microwave-treated VTM. As previously mentioned, intergranular fractures of microwave-treated VTM would improve the liberation of minerals and hence increase separation efficiency. To verify these results, we ground the untreated and microwave-treated VTM in an experimental ball mill. According to Fig. 12, the Fe grade of the magnetic fraction (same magnetic field intensity) of microwave-treated VTM was approximately 1% higher than that of untreated VTM when ground to the same particle size (56wt% at < 0.074 mm).

Generally, on the basis of energy expenditure alone, microwave treatment to enhance the grindability and dissociation of the VTM ore was not cost effective. Enhancing grindability results in variations in the comminution processing, which could reduce the grinding energy consumption. If the VTM ore is accessible to grind finely, it could cause less wear of the mill equipment [24]. Enhanced grindability could also lead to an increase in processing capacity and to a reduction in the number of circulations. These changes through microwave treatment could be conducive to decreasing energy consumption for grinding VTM ore. Furthermore, enhanced dissociation of the ground product of

VTM ore would reduce the level of difficulty of the beneficiation process and may result in a better ore-dressing index.

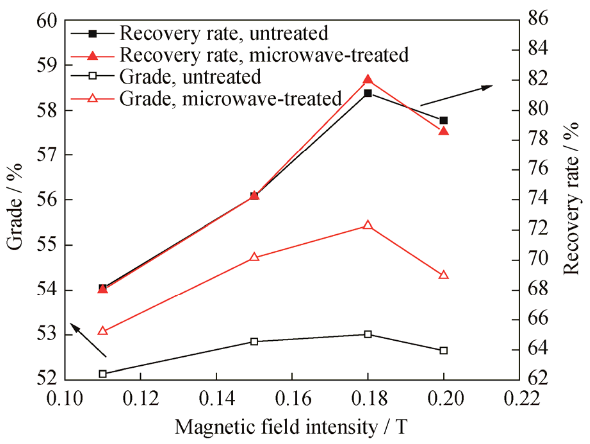

Fig. 11. Fe grade and recovery rate of magnetic fraction of untreated and microwave-treated VTM (140 s) ground for 2 min under different magnetic field intensities.

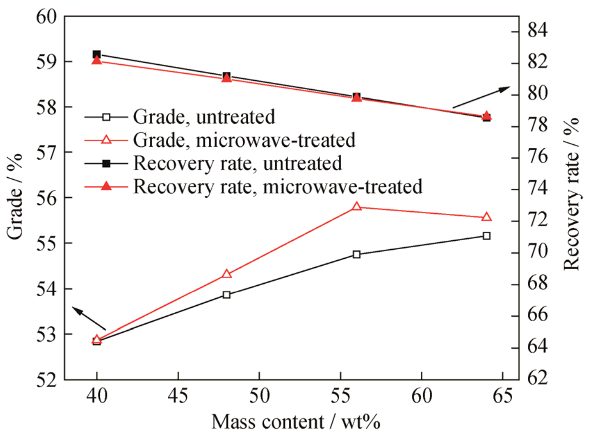

Fig. 12. Fe grade and recovery rate of magnetic fraction of untreated and microwave-treated VTM (140 s) under different grinding fineness (< 0.074 mm).

4. Conclusions

In this study, the influence of microwave treatment on grinding and dissociation characteristics of VTM was investigated. After microwave treatment, microfractures appeared in ore particles and crystallinity increased with increasing microwave heating time. The vibration bands of metallic ions and Si−O gradually increased in intensity after microwave irradiation. In addition, after processing by microwave treatment, the grindability of VTM was enhanced, thus increasing the production of finer particles. When VTM was irradiated at a suitable microwave power level, prolonging the microwave heating time appropriately could produce higher rates of weight percent of fine-ground product. The particle size distributions of the fine-ground product only showed a slight change after microwave heating. Microwave treatment could improve the dissociation of the VTM ore, thus increasing the efficiency of magnetic separation of ground products and improving the Fe grade of the magnetic fraction. The Fe grade of the magnetic fraction of the microwave-treated VTM was 1.72% higher than that of the raw ore.

Acknowledgements

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