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Letter

Rapid synthesis of rutile TiO_2 powders using microwave heating

ABSTRACT

In this present study, the thermal stability, crystal structures, and molecular structure of the sulfate titanium slag and the microwave treated samples were also analyzed using TG, XRD, and Raman spectrum, respectively. The reaction mechanism of oxidation reaction and the polymorphic transformation of the sulfate titanium slag were systematically investigated to identify the reaction processes. The effects of both temperature and time on the structure and chemical properties of the microwave treated samples were systematically investigated. The analysis results of the $FeO-TiO_2-TiO_{1.5}$ phase diagram showed that the oxidation reactions were occurred along the line of anosovite ($Fe_3Ti_3O_{10}$)-low valent titanium-TiO_2. The results of XRD showed that the anosovite phase of the sulfate titanium slag were transform to the rutile TiO_2 phase under microwave heating at 950 °C for 60 min. The Raman spectrum results demonstrate that the vibration bands of low-valent titanium in the sulfate titanium slag were disappeared, and the vibrations bands of rutile TiO_2 were formed after microwave heating processing. All the microwave treated samples have typical tetragonal structures that are well-crystallized.

Keywords:
Sulphate titanium slag
Microwave heating processing
Oxidation reaction
Polymorphic transformation

1. Introduction

Titanium dioxide (TiO_2), the main application areas are coatings, plastics, ink and paper, which paints accounted for 60%, plastics for 20%, paper accounts for 14%, other (including the field of cosmetics, chemical fiber, electronics, ceramics, enamel, welding rod, alloy and glass, etc.) accounted for 6% [1]. The applications of titanium dioxide in industrial are becoming increasingly widespread [2]. Because titanium dioxide non-toxic, than the white lead is superior, all kinds of titanium dioxide powder used to replace almost all of white lead and zinc white [3,4]. Therefore, over 4 million tons of titanium dioxide is used worldwide every year for a wide array of common applications.

Titanium dioxide has rutile (Rutile TiO_2, R-type) and anatase (Anatase TiO_2, A-type), which two kinds of structures, rutile crystal structure of dense, relatively stable, and optical activity is small, so weather is good, while there is a high hiding power, color power consumption and thus have a better application performance, access to a wider range of applications [5–12]. The phase transformation of anatase to rutile is influenced by the several experimental conditions, such as roasting temperature, particle size of samples, and synthetic method of dioxide. Rutile TiO_2 is produced from ilmenite, sulfate titanium slag or titanium slag [13–16]. The titanium pigment is extracted by using either sulfuric acid (sulfate process) or chlorine (chloride route). The sulfate process employs simpler technology while the chloride route produces a purer product [17–20]. Titanium dioxide production and applications should take into account the influence of the shortage of high quality titanium resources and reducing environmental pollution [21–23].

Many techniques have been used to treat the minerals ores or materials, which are environmentally acceptable with reasonable procedures to treat various solutions and solids obtained [24–32]. Therefore, an exploration of a new technology, with less energy consumption and higher minerals recovery, and is very suitable for application in commercial scale operation, which is necessary for sustainable development [33–41].

Microwaves are electromagnetic waves that have a frequency range from around 0.3 GHz (there is no actual specified lower frequency limit) to 300 GHz with corresponding wavelengths ranging from 1 m to 1 mm [42–46]. At the moment, three different microwave frequencies are available for industrial microwave heating. The frequency 915 MHz is mainly used for defrosting and heating of large scale materials [47–52]. The most widely used 2.45 GHz is most household and industrial systems. Since early 2002 the new frequency 5.8 GHz is available for industrial use. It is especially advantageous for small pieces and materials that are difficult to heat with the lower frequencies [53,54]. Recently, microwave energy has been widely used in several fields of applications on both research and industrial processes [55–63]. Many successful examples illustrate this application, including drying product of chemical industry, preparing active carbon, microwave assistant milling, and vulcanizing rubber. The microwave absorbing property of materials and minerals is an important physical indicator in the fields of microwave chemistry, microwave detection, and microwave processing [64–70].

It is well known that containing titanium resources of the ores show the good microwave-absorbing characteristics. Guo et al. [71] investigated the microwave absorbing characteristics of

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mixtures of different carbonaceous reducing agents and oxidized ilmenite. It has been shown that the microwave absorbing characteristic of these carbonaceous reducing agents (coconut-based activated carbon, coke and graphite) were all better than that of oxidized ilmenite under the conditions of particle size of 175 μm–147 μm. Chen et al. [72] investigated the influences of microwave irradiation on the dissociation behavior and structural characterization of ilmenite ore. The XRD, SEM and FT-IR analysis results indicated that the crystal structures, microstructure, and surface chemical functional groups of microwave treated ilmenite ore are better than those of ilmenite ore. Chen et al. [73] investigated the effect of three major influencing parameters microwave power, time and mass of sample on the combined microwave pretreatment and magnetic separation of ilmenite through application of process optimization technique response surface methodology. The optimum experiment conditions were found to be 2400 W of microwave power, 30.11 min of time and 44.80 g of sample mass, resulting in an experimental recovery ratio of 68.73%.

The objective of this study is to investigate the structure and chemical properties of the sulfate titanium slag in microwave heating processing using different techniques. The thermal stability, crystal structures, and molecular structure of the sulfate titanium slag and the treated samples, which before and after microwave heating processing were also analyzed using TG, XRD, and Raman spectrum, respectively. The reaction mechanism of oxidation reaction and polymorphic transformation of the sulfate titanium slag was systematically investigated to identify the reaction processes.

2. Experiment

2.1. Materials

The sulfate titanium slag was obtained from Kunming city, Yunnan Province, China. The raw materials were prepared from the ilmenite ores by carbothermal reduction in an electric arc furnace. The chemical compositions of the sulfate titanium slag were shown in Table 1. The sulfate titanium slag with 72.33% of TiO_2, 2.34% of Ti_2O_3, and 11.15% of TFe, also contains 9.57% of SiO_2, 1.52% of MnO, 2.21% of Al_2O_3, 0.50% of CaO, and minor elements such as S, P and C. The sulfate titanium slag and the microwave treated samples were analyzed for element content by the method in accordance with the recommended methods of National Standard of the People's Republic of China (GB/T).

2.2. Characterization

Thermogravimetry analysis for oxidation of the sulfate titanium slag was performed using a STA 409 thermal analyzer (Netzsch, Germany). For that purpose about 20 mg of the substances were filled in corundum containers and heated at a constant rate of 10 °C/min under flowing argon. The thermal decomposition was followed from 25 °C up to 1000 °C. For the TG data a baseline correction was applied, and onset and end temperatures of the thermal effects were taken from the differentiated TG curve following common procedures using the software supplied with the analyzer. The crystalline phase of the sulfate titanium slag, and the synthetic rutile, which were prepared using microwave irradiation, was also studied on the powder x-ray diffractometer (XRD, D/Max 2200, Rigaku, Japan) in CuKα radiation (λ = 1.5418 Å) with a nickel filter. The anode voltage and the current were 35 kV and 20 mA, respectively. The data were collected between 5° and 100° the scattering angles (2θ), with the scanning rate of 0.25°/min. The 2θ values of the samples corresponding to different X-ray peaks were identified and calculated, which silicon powder was used as an internal standard and Rietveld refinement method was used to determine the crystalline structure by powder diffraction data. The Raman spectra of samples were performed at room temperature using a confocal microprobe Raman system (Renishaw Ramascope System 1000, UK) with an air-cooled charge-coupled device (CCD) detector. A 514-nm argon laser was used for excitation. Backscattered Raman signals were collected through a microscope and holographic notch filters in the range of 100–1000 cm^{-1} with a spectral resolution of 2 cm^{-1}. The Raman system was calibrated against the emission lines of neon. The laser power on the sample surface was 20 μW to prevent irreversible thermal damage the samples, the spot diameter was 5 μm and the typical collection time of one measurement was 10 s.

Table 1
Chemical composition of the sulfate titanium slag.

TiO_2	Ti_2O_3	TFe	S	P	C	Al_2O_3	SiO_2	MgO	CaO
72.33	2.34	11.15	0.049	0.014	0.049	2.21	9.57	1.52	0.50

2.3. Instrumentation

In present study, the microwave heating device used was made by the Key Laboratory of Unconventional Metallurgy, Ministry of Education, Kunming University of Science and Technology, China. The schematic diagram of the microwave reactor was shown in Fig. 1. The microwave heating device provides two choices of control model, which containing the automatic mode and the manual mode for microwave heating processing. It was mainly composed of the microwave generators (magnetron and waveguide), a microwave resonant cavity, a power controller, a matched load, a quartz tube, a temperature sensor, a mixer, a weight measurement system, a gas generator and a flow meter, a cooling system and a computer control system. Self-made microwave reactor has a multi-mode cavity, with a continuous controllable power capacity. Microwave power was generated by two magnetrons at 2.45 GHz microwave frequency and 1.5 kW microwave power, which was cooled by water circulation. A gas generator was linked to the microwave heating device. It could provide protect gas for maintaining the inert atmosphere in the quartz tube of the microwave heating unit.

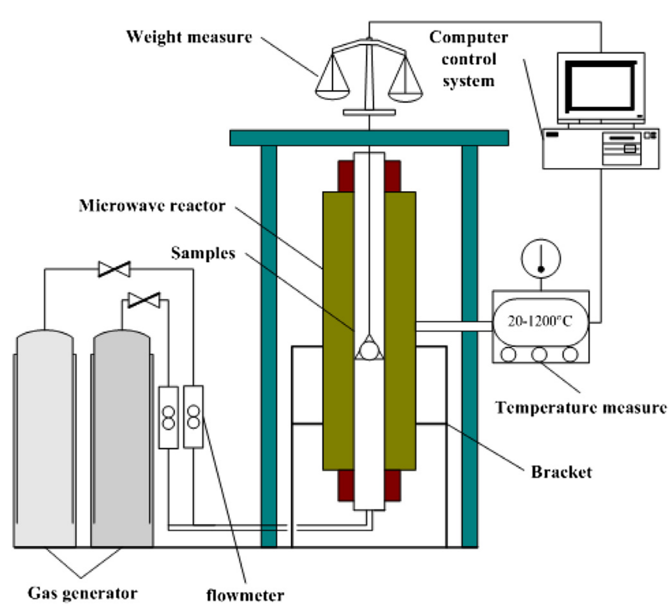

Fig. 1. Schematic diagram of microwave heating apparatus.