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Letter

Investigation on phase transformation of titania slag using microwave irradiation

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ABSTRACT

The work addresses phase transformation of titania slag using microwave irradiation. Properties of samples before and after microwave irradiation including thermal stability, crystal structures, microstructure, surface chemical functional groups and molecular structures, have been investigated by TG/DTA, XRD, SEM, FT-IR and Raman, respectively. The results of TG/DTA showed that titania slag have two phase transformation, one at 578.0 °C and another at 850.0 °C. It was confirmed that at roasting temperature in excess of 600 °C, anatase starts to transform as rutile. The property changes can be attributed to microwave irradiation, which causes the crystal transformation.

1. Introduction

Titanium is the ninth most abundant chemical element and the fourth most abundant usable metallic element in the Earth's crust [1]. Rutile, anatase and brookite have higher titanium contents than other titaniferous minerals, which are in fact trimorphs [2,3]. These three distinct minerals are composed of different crystalline forms, but with similar chemical structure [4,5]. Titania pigment is manufactured either using the sulfate process, in which the ore is reacted with concentrated sulfuric acid, or the chloride process, in which the ore is chlorinated to form titanium tetrachloride, which are then re-oxidized to form pigments [6]. Rutile TiO_2 is more popularly utilized due to its high refractive index, whiteness, brightness, thermal stability and chemical inertness, which finds wide range of applications, including the manufacture of white pigment [7,8]. About 60% of natural rutile is used for the manufacture of titanium metal, since they are light in weight, high in tensile strength and corrosion-resistant, widely used in the manufacture of aircraft, spacecraft and medical prostheses [9,10]. The increasing use of chloride process for producing titanium dioxide pigments has motivated the search for a more abundant and cheaper source of raw material than the presently used titania slag. Hence, development of more efficient and effective method to utilize titania slag is imperative.

Microwave irradiation technology is one of effective routes in realizing energy saving and green production [11]. The main difference between microwave heating and conventional heating systems is in the way the heat is generated [12]. Compared with conventional heating techniques, the main advantages of microwave processing is reduction in processing time and energy consumption, since microwave heating is both internal and volumetric [13]. Since microwave heating is energy efficient and facilitate rapid and uniform heating, it is favorable to the process economics. Microwave energy has been widely used in several fields of applications both at research as well as commercial scale industrial mineral processing [14,15]. Although microwave irradiation has been utilized to treat titania slag for preparation of synthetic rutile, relevant literature is very limited [16].

The objectives of present work are to: (1) preparation of synthetic rutile from high titania slag under microwave irradiation; and (2) assess properties of samples before and after microwave irradiation, including thermal stability, crystal structures, microstructure, surface chemical functional groups and molecular structures, systematically.

2. Experiment

2.1. Materials

Titania slag was obtained from Kunming city, Yunnan province, China. The slag contains 72.33% TiO_2, 17.79% Ti_2O_3, and 5.26% FeO. The slag also contains 1.04% MnO, 2.75% Al_2O_3, 2.30% MgO, 2.57% SiO_2 and minor elements such as S, P and C. The titania slag was analyzed for element content in accordance with the National Standard of the People's Republic of China (GB/T).

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2.2. Characterization

The thermogravimetry and corresponding differential thermal analysis were carried out simultaneously using a thermal gravimetric analyzer (NETZSCH STA 409, Germany). X-ray diffraction (XRD) patterns were recorded on a X-ray diffractometer (D/Max 2200, Rigaku, Japan) using Cu Kα radiation (λ = 1.5418 Å) and a graphite monochromator for the diffracted beam. 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}. Fourier transformation infrared spectra were collected using FT-IR spectrometer (8700, Nicolet, USA). The angle of incidence of the IR beam was 45° and 100 scans were collected at a resolution of 4 cm^{-1} and averaged using the OMNIC spectroscopic software. A scanning electron microscope (XL30ESEM-TMP, Philips, Holland) was used to observe the microstructure morphology of the titania slag and synthetic rutile processed.

2.3. Instrumentation

The microwave irradiation experiments were carried out in a self-made microwave muffle furnace. An industrial microwave muffle furnace typically consists of a magnetron to produce the microwaves, a waveguide to transport the microwaves, a resonance cavity to manipulate microwaves for a specific purpose, and a control system to regulate the temperature and microwave power. The power supply of the microwave muffle furnace was two magnetrons at 2.45 GHz frequency and 1.5 kW power, which was cooled by water circulation. The inner dimensions of the multi-mode microwave resonance cavity were 260 mm in height, 420 mm in lengthen and 260 mm in width. The temperature is measured using a Type K thermocouple, placed at closest proximity to the sample. Thermocouple provides feedback information to the control panel that controls the power to the magnetron, controlling the temperature of the sample during the microwave irradiation process in order to prevent the sample from overheating.

2.4. Procedure

100 g of titania slag was loaded on a ceramics boat and placed inside a stainless steel tubular reactor which was heated to a temperature of 120 °C at a heating rate of 5 °C/min. The samples were held at 120 °C for duration of 120 min in order to completely remove the moisture from the samples. The dried samples were transferred to the microwave irradiation apparatus and heated to 950 °C and held at that temperature for duration of 60 min.

3. Results and discussion

The TG and the DTA curves of the samples are shown in Fig. 1. According to TG/DTA curves, titania slag has three weight change stages. The first step is a dehydration step, characterized by an endothermic DTA peak in the temperature range 100–110 °C. The weight loss accompanying this step amounts to about 0.08% in accordance with calculated weight loss of 0.09% attributed to the complete dehydration [17,18]. The $Fe_3Ti_3O_{10}$ decomposed in the second step, indicates weight gain of 0.87% due to the formation of anatase TiO_2 from $Fe_3Ti_3O_{10}$, accompanied by a very sharp exothermic DTA peak at 578.0 °C. Anatase TiO_2 is thermally stable up to 600 °C, which transformed in the third step with weight gain of 2.99% in agreement with the formation of rutile TiO_2, characterized by an exothermic DTA peak at 850 °C. The final product corresponds to synthetic rutile. TG/DTA curves also indicate the corresponding temperatures to the theoretical weight gain, which formed the basis for selecting the minimum roasting temperature of 950 °C and 60 min.

On the basis of experimental results, the following mechanism of the weight gain of titania slag could be proposed:

$$2Ti_2O_3 + O_2 \rightarrow 4TiO_2 \quad (1)$$

$$2Ti_3O_5 + O_2 \rightarrow 6TiO_2 \quad (2)$$

The following mechanism of decomposition reaction of $Fe_3Ti_3O_{10}$ and the anatase–rutile crystal transformation of TiO_2 could be proposed:

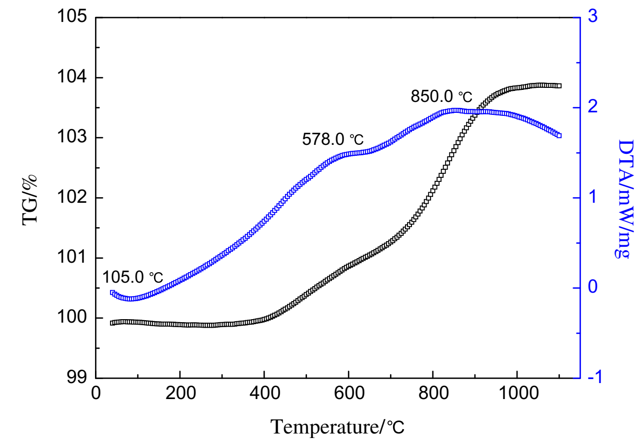

Fig. 1. TG/DTA curves of titania slag.

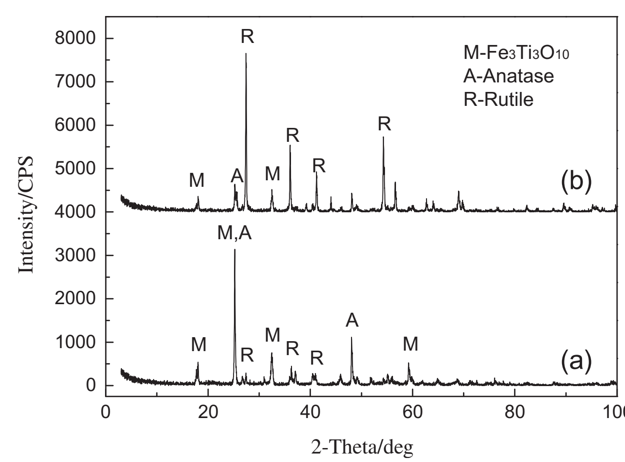

Fig. 2. XRD of titania slag before and after microwave irradiation at 950 °C for 60 min: (a) raw materials and (b) microwave treated samples.

$$Fe_3Ti_3O_{10} \rightarrow 3TiO_2\,(\text{Anatase}) + Fe_3O_4 \quad (3)$$

$$TiO_2\,(\text{Anatase}) \rightarrow TiO_2\,(\text{Rutile}) \quad (4)$$

The crystal structures of titania slag are characterized by XRD, and the results are illustrated in Fig. 2. It is found from Fig. 2a that the main phase of titania slag is $Fe_3Ti_3O_{10}$ and the anatase TiO_2 match well with those of reference XRD data. However, XRD pattern shows that rutile TiO_2 also exist in the samples. These results indicate that titania slag consists of multi-crystalline phases. The strongest diffraction peaks of $Fe_3Ti_3O_{10}$ and anatase TiO_2 are observed around 25.45° and 25.28°, respectively. Fig. 2(b) shows the X-ray diffraction of pattern of titania slag after microwave irradiation at 950 °C for 60 min [19,20]. It can be observed from Fig. 2b that the diffraction peaks are smooth and clear, and the strong peaks of microwave treated samples appear at 27.44°, and hypo-strong peaks appear at 36.09°, 41.25° and 54.33°, which are similar to the standard PDF card of rutile TiO_2. The narrow diffraction peaks also indication that the samples have a very good crystalline structure [21]. Based on the above results, beginning of the transformation of anatase TiO_2 into rutile can be confirmed at temperature in excess of 600 °C [22,23]. Furthermore, the intensity of anatase phase decreases while the intensity of rutile phase increases with increasing microwave roasting temperature. At a microwave roasting temperature of 950 °C, the anatase TiO_2 transformation into rutile TiO_2 is complete.