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A novel method of synthesis and investigation on transformation of synthetic rutile powders from Panzhihua sulphate titanium slag using microwave heating

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ABSTRACT

A novel microwave roast process for synthesizing rutile TiO_2 having high crystallinity from Panzhihua sulphate titanium slag is developed in the present work. Properties of samples at various stages of reactions including the crystal structure, microstructure and molecular structure, were investigated by X-ray diffraction (XRD), scanning electron microscope (SEM) and Raman techniques, respectively. The work also addressed the phase transformation of sulphate titanium slag before and after microwave heating. The result of XRD showed that under the microwave roasting process, the sulphate titanium slag was decomposed following acidification of the sodium titanates. The SEM analysis showed morphology transformations during the whole process and the short rod-like structure of rutile after the treatment. The Raman spectroscopy demonstrated that the peaks of 141 cm^{-1}, 254.8 cm^{-1}, 428.8 cm^{-1}, and 606.2 cm^{-1} corresponded to the characteristic patterns of rutile TiO_2. Based on the above results, this process could be an efficient way for rutile TiO_2 preparation utilizing Panzhihua sulphate titanium slag.

1. Introduction

Titanium is the ninth most abundant chemical element on the earth that plays an important role in the manufacture of paint, plastics, paper, and cosmetics industries [1,2]. Rutile, anatase and brookite are the main forms existing in nature with higher titanium content than other titaniferous minerals [3–5]. TiO_2 pigment is commonly manufactured either by the sulphate process or the chloride process. During the sulphate process [6], the raw materials are dissolved in concentrated sulphuric acid to hydrolyze the titanium, which are further calcined into titanium dioxide. The chloride process involves chlorinating the ore to form titanium tetrachloride which are then re-oxidizing to form pigments [7]. Commercially the chloride process is more attractive than sulphate process for production of TiO_2 pigment, since it is environmentally benign [8]. However, limitations in the availability of natural rutile have resulted in attempts to utilize cheaper sources of raw materials for chloride process [9]. Hence, it is imperative to develop more efficient and effective methods to utilize titanium slag.

Numbers of studies have been reported to upgrade titanium slag, so as to utilize the low grade titanium slag. Oi et al. have proposed sodium hydroxide based decomposition process for synthesizing rutile TiO_2 [10]. The titanium slag was decomposed the NaOH/KOH binary molten salt system to form the intermediate Na_2TiO_3, which was treated with warm water and then dissolved in acids to form precipitate of hydrated TiO_2, which was calcined to form rutile TiO_2. Nayl et al. have heated ilmenite slag in 4 M NH_4OH solutions to 150 °C, to form high purity titanium oxide [11]. Alternatively, Middlemas et al., have utilized a novel process of treating titania slag with alkaline roast-leach method to synthesize rutile TiO_2 [12]. This process involved decomposition of titanium slag to form sodium titanate followed by five stages which include washing, leaching, solvent extraction, hydrolysis and calcination.

Microwave irradiation technology is an emerging route for green production which consumes far less energy as compared to conventional heating techniques. Microwaves are electromagnetic waves whose frequency ranges from about 0.3 to 300 GHz with corresponding wavelengths ranging from 1 m to 1 mm [13–19]. Under the microwave irradiation, the energy is transmitted to molecules or atoms selectively through internal dielectric loss of materials. This enables energy

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conversion mode in a micro-area of materials to obtain rapid energy accumulation [20]. Nowadays, microwave energy is being widely used in laboratory scale as well as for commercial industrial manufacturing processes [21–23].

In the present work, a microwave roast-leach process is developed to produce high quality rutile. The primary focus is to investigate the influence of microwave heating on the roast-leach process to produce synthetic rutile from Panzhihua sulphate titanium slag. Furthermore, the crystal structure, microstructure and molecular structure of the sulphate titanium slag at various stages during reactions were analyzed by X-ray diffraction, scanning electron microscope and Raman techniques, respectively.

2. Experimental

2.1. Materials

The Panzhihua sulphate titanium slag utilized in the present work was supplied by Panzhihua Iron and Steel Research Institute (Panzhihua city, Sichuan Province, P.R. China). The chemical composition of sulphate titanium slag is presented in Table 1. And the mesh analysis of the titanium slag is presented in Table 2. The sulphate titanium slag contains 71.66% TiO_2 and 7.70% TFe. The slags also contain 3.69% Al_2O_3, 2.35% MgO, 2.63% SiO_2, 0.37% CaO, and minor elements such as S, P and C. The XRD pattern of sulphate titanium slag was displayed in Fig. 1. It was found from Fig. 1 that the main phases of sulphate titanium slag were $M_xTi_{3-x}O_5$ ($0 \le x \le 2$) and the anatase TiO_2 (JCPDS card No. 84-1285). $M_xTi_{3-x}O_5$ ($0 \le x \le 2$) belongs to the typical concise empirical chemical formula of pseudobrookite group with M = Ti^{3+}, Fe^{3+}, Mg^{2+}, etc. [24,25]. The XRD patterns also indicate that the raw materials consist of a small amount of rutile TiO_2 (JCPDS card No. 21-1276).

2.2. Characterization

Various phases present in samples were identified using the powder X-ray diffraction(Rigaku D/Max 2200 X, Japan) using CuKα radiation(λ = 1.5418 Å). The voltage and anode current operated were 35 kV and 20 mA respectively. The phase identification and composition were also verified by making comparison with the Joint Committee on Powder Diffraction Standards (JCPDS) reference patterns. Analytical scanning electron microscope (XL30ESEM-TMP, Philips, Holland) operated at 20 kV in a low vacuum also contributed to the understanding of the microscopic processes taking place at various stages of reactions. The Raman spectra of samples were performed at room temperature using Raman system (Renishaw Ramanscope System 1000, UK). Backscattered Raman signals were collected through a microscope and holographic notch filters in the spectrum scattering detection region ranges ranged from 100 cm^{-1} to 1000 cm^{-1}.

2.3. Experimental procedure

A microwave roasting process for the production of rutile TiO_2 using sulphate titanium slag was proposed based on the Na_2CO_3 decomposition process. A block flow diagram of the novel process is shown in Fig. 2. The sulphate titanium slag was mixed with Na_2CO_3 slag at a ratio of 0.55:1. 10 g of mixture was roasted in a microwave furnace at 850 °C for 2 h. After roasting the sample was counter currently washed with water. The washed solid was then digested with 35% boiling sulfuric acid at a ratio(S/L) of 1:5 for 6 h. Finally, the intermediate product was calcined at 950 °C by microwave heating for 1 h to achieve complete crystalline growth.

Table 1
Chemical compositions of the sulphate titanium slag.

Composition	TiO_2	TFe	Al_2O_3	MgO	SiO_2	CaO	S	P	C
Mass%	71.66	7.70	3.69	2.35	2.63	0.37	0.12	0.018	0.017

Table 2
analysis of the sulphate titanium slag.

Particle size/μm	>180	150–180	120–150	96–120	75–96	48–75	<48
Content/%	32.4	24.8	10.2	12.2	9	7	4.4

The chemical reactions involved in the process of formation of titanates can be represented by equations as follows,

$$FeTi_2O_5 + 2Na_2CO_3 = 2Na_2TiO_3 + FeO + 2CO_2 \quad (1)$$

$$MgTi_2O_5 + 2Na_2CO_3 = 2Na_2TiO_3 + MgO + 2CO_2 \quad (2)$$

$$FeTiO_3 + Na_2CO_3 = Na_2TiO_3 + FeO + CO_2 \quad (3)$$

$$TiO_2 + 2Na_2CO_3 = Na_2TiO_3 + CO_2 \quad (4)$$

$$Al_2O_3 + Na_2CO_3 = 2NaAlO_2 + CO_2 \quad (5)$$

$$SiO_2 + Na_2CO_3 = Na_2SiO_3 + CO_2 \quad (6)$$

Accordingly the roasted products contain titanium in the form of Na_2TiO_3 which hydrolyses to form a precipitate of hydrated TiO_2 and then calcined to produce synthetic rutile. The following equation gives the chemical reaction during the hydrolysis.

$$Na_2TiO_3 + 2H^+ = TiO_2 + 2Na^+ + H_2O \quad (7)$$

3. Results and discussion

3.1. Characterization by XRD

The XRD pattern of soda ash roasted sulphate titanium slag with microwave at 850 °C for 120 min is shown in Fig. 3(a). Clearly in the presence of Na_2CO_3 the formation of non-stoichiometric Na-Fe-Ti-O and Na-Mg-Ti-O phases in roasted products is seen in Fig. 3(a), which is different from the products shown in reactions (1) through reactions (4). This can only be attributed to the complexity of the raw materials. Besides the amount of sodium carbonate may be insufficient, resulting only in a partial conversion. By comparing Fig. 1 and Fig. 3(a), the results show that the solid phase reaction occurs during microwave heating after adding Na_2CO_3 and the main impurities in raw materials change to a series of new soluble phases. Fig. 3(b) shows the X-ray diffraction pattern of sulphate titanium slag after acid leaching process.

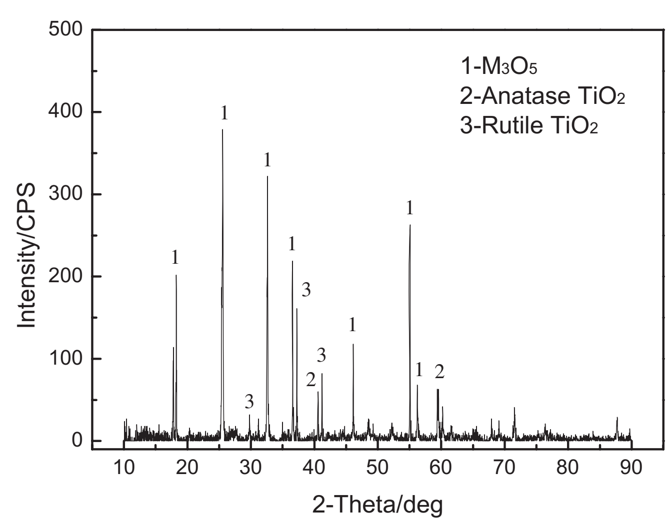

Fig. 1. XRD of Panzhihua sulphate titanium slag.