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Preparation and purification of titanium carbide via vacuum carbothermic reduction of ilmenite

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ABSTRACT

An economical route has been developed to prepare high purity titanium carbide from Panzhihua ilmenite, which has high contents of Mg and Si. In this paper, high purity (>99 wt%) TiC particle was prepared by vacuum carbothermal reduction followed with acid leaching and alkali leaching processes. The current process has a lower reaction temperature, and a shorter reaction time, meanwhile the used raw materials are much cheaper than the industrial method of preparing TiC which used TiO_2 and C as the raw materials. Effects of atmosphere, reduction temperature and carbon ratio were studied and the purification mechanisms of elements Mg, Mn, Ca, Si, Al were put forward. Mg and Mn could be separated in gaseous state during vacuum carbothermal reduction. Al was reduced to Al_4C_3 after reduction and then was removed in acid leaching process. Meanwhile, CaO was also removed in the acid leaching process. SiO_2 was reduced to the dissolved silicon in liquid iron firstly, then formed amorphous silicon after acid leaching, and finally was removed in alkali leaching process. The as-prepared TiC powder had a narrow particle size distribution within 1–20 μm and D_v50 was 5.29 μm.

1. Introduction

Titanium carbide with face-centered cubic structure of NaCl is a promising engineering ceramic which has attractive physical and chemical performances. Due to its high melting point, high chemical and thermal stability, excellent wear resistance and hardness, titanium carbide has been widely applied in various fields, such as cutting tools, grinding wheels, wear-resistant coatings and turbine engine seals [1–6]. For all these applications, it is of practical interest to produce titanium carbide powders with a fine particle size and narrow size distribution [7].

Nowadays, various methods have been employed to synthesize titanium carbide. such as direct carbonization of titanium metal or titanium hydride [8–13], mechanical alloying [14–16], carbothermal reduction of titanium dioxide [17–20], carbothermal reduction of $TiCl_4$ [21], solation-gelation(S-G) method [22–26], electrochemistry method [27], chemical vapor deposition [28]. However, most studies about the preparation of TiC used pure reagents as the raw materials, which results in a high production cost of TiC. In China, more than 90 wt% of ilmenite is located in Panzhihua, Sichuan Province [29,30]. If ilmenite could be directly used as raw materials to prepare TiC, the production cost will be greatly reduced. However, the contents of MgO and SiO_2 in Panzhihua ilmenite is as high as 6 wt% and 3.5 wt%, respectively [31–34]. Gou found that $MgAl_2O_4$ and Mg_2SiO_4 were generated in the products after carbothermic reduction process and could not be separated from titanium carbide by leaching process [35,36]. Other investigations have been proposed to prepare titanium carbide using carbothermal reduction of ilmenite [37,38]. However, the removals of Si and Mg were also the biggest problems.

In industrial production process of TiC, TiO_2 is used as raw material, and the solid-solid reaction between TiO_2 and C needs 10–20 h to finish at 1973–2373 K [39]. Compared with the traditional method, the present work used ilmenite as raw material, which has a much lower cost. Besides, when the reaction temperature was above the eutectic temperature of 1427 K in Fe–C binary system, part of carbon would dissolve into Fe to form a liquid phase, which made the liquid Fe as a diffusion channel of carbon to the reaction interface. There will be better dynamic conditions than the solid-solid reaction between TiO_2 and C in industrial preparation process of TiC [38]. This good dynamic condition substantially decreased the reaction time and lowered the reaction temperature.

In this paper, a new purification route to remove the impurity

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Table 1
Chemical compositions of Panzhihua ilmenite (wt. %).

Component	FeO	Fe_2O_3	TiO_2	MgO	SiO_2	Al_2O_3	CaO	MnO	Total
Content	36.85	5.59	45.34	5.76	3.46	1.35	0.96	0.69	100

elements Mg, Mn, Al, Si was put forward. TiC particle was prepared by vacuum carbothermal reduction followed with acid leaching and alkali leaching processes. Effect of atmosphere, reduction temperature and carbon ratio were studied and the purification mechanism was also discussed in detail.

2. Experimental

Activated carbon, ilmenite, hydrochloric acid solution and sodium hydroxide solution were used in the experiment. The activated carbon (analytical reagent), hydrochloric acid solution (analytical reagent) and sodium hydroxide (analytical reagent) were supplied by Sinopharm Chemical Reagent Beijing Co., Ltd, Beijing, China. The ilmenite was supplied by Panzhihua Iron and Steel (Group) Co., Ltd, Panzhihua, China. Its compositions were detected by chemical analyses and shown in Table 1.

Ilmenite and activated carbon were mixed in a blender with a rotating speed of 11000 rpm. The powders with addition of polyvinyl alcohol solution (PVA, 3 wt%) were compressed into cylindrical pellets (Φ18 mm × 6 mm) by uni-axial pressing in a stainless steel die under 230 MPa. Then the green pellets held in alumina crucibles were put into an electric resistance furnace with a pressure control system. The samples were heated to the desired temperature at a heating rate of 5 K min^{-1} and then were cooled to the ambient temperature at a cooling rate of 5 K min^{-1} after reacting for 4 h. Detailed experimental parameters were shown in Table 2. The obtained products were slightly crushed and then put into the hydrochloric acid solution (5 wt%) at ambient temperature for 3 h with electromagnetic stirring. Lower precipitation was filtered, washed by deionized water for several times, and then were dried at 373 K in a draught drying cabinet (DHG-9030A, Shanghai Yiheng Instruments CO, Ltd., Shanghai, China). The obtained powders were put into sodium hydroxide solution (10 wt%) for 2 h with electromagnetic stirring. TiC powders were obtained after filtering, washing, drying. Products were examined by X-ray

Table 2
Experimental conditions of carbothermic reduction in vacuum.

Group	Mass ratio (carbon: ilmenite)	Temperature/K	Pressure/Pa	Atmosphere	Holding time/h
No. 1	0.391:1	1673	101325	Argon	4
No. 2	0.391:1	1673	10	Argon	4
No. 3	0.391:1	1673	10	Air	4
No. 4	0.391:1	1773	10	Air	4
No. 5	0.424:1	1673	10	Air	4
No. 6	0.424:1	1773	10	Air	4
No. 7	0.456:1	1673	10	Air	4
No. 8	0.456:1	1773	10	Air	4
No. 9	0.358:1	1773	10	Air	4
No. 10	0.365:1	1773	10	Air	4
No. 11	0.371:1	1773	10	Air	4
No. 12	0.378:1	1773	10	Air	4
No. 13	0.385:1	1773	10	Air	4

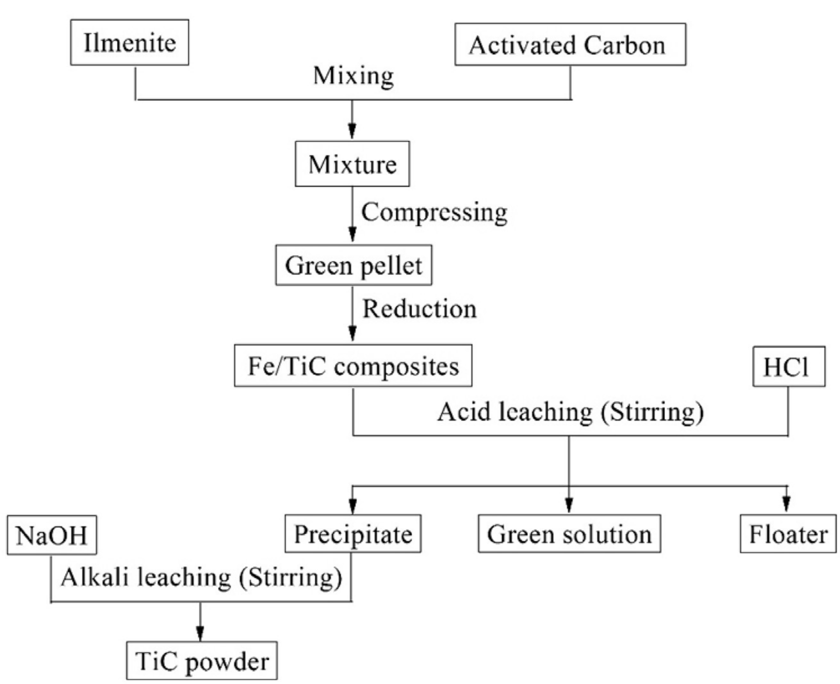

Fig. 1. Experimental procedure flowchart.