Review of TiO_2-Rich Materials Preparation for the Chlorination Process

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Abstract Chlorination process is a clean and efficient way to manufacture of titanium dioxide pigment. However, the limited natural rutile promotes the investigation on the upgrading of ilmenite ore into titanium-rich materials. The principle and producing situation of some production methods of TiO_2-rich materials preparation for the chlorination process are discussed. The advantage and disadvantage of the Reduction smelting produces titaniferous slag, Carbothermal reduction-nitridation, Acid leaching, and Reductive leaching produce synthetic rutile are also summed in this paper. This paper presents a review of these technologies and carbothermal reduction-nitridation method is recommended to deal with Panzhihua ilmenite ore to meet the needs of the titanium dioxide pigment production by chlorination process.

Keywords Rich titanium materials · Chlorinate · Carbothermal reduction-nitridation

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Introduction

Panzhihua, China is considered a significant resource of ilmenite, and makes up a large proportion (35%) of the world's total reserves [1]. Unfortunately, Panzhihua ilmenite has high contents of calcium and magnesium. The main component of Panzhihua ilmenite is $FeTiO_3$, the main features of which are (1) its structure is dense, optionally poor, and difficult to separate TiO_2 to other constituents; (2) the content of TiO_2 is low compared to rutile. Panzhihua ilmenite has a high impurity content, particularly MgO content [2].

Although ilmenite can be directly used as the raw material such as titanium dioxide or titanium sponge, it is lengthy, costly and produces large amounts of by product, which results in some environmental problems [3]. The technology in China is facing increasing pressure from government. Therefore, the development of chlorination technology is imperative. The production of Chlorinated titanium dioxide and titanium sponge require high-quality titanium-rich materials, therefore the preparation of material for Panxi ilmenite mainly is used in chlorinated titania process. Preparing chlorinated rich titanium materials not only for China's titanium industries has a decisive significance, but also for the development of metallurgical technology has great significance.

Preparation of Rich Titanium-Rich Materials

Reduction Smelting

The reduction smelting of ilmenite is in the 1600–1800 °C, then titanium enriches in slag phase, so we call it as titanium slag and high content of titanium is called high titanium slag. Reduction smelting which includes open arc furnace, semi-closed arc furnace and enclosed arc furnace is a commonly used method. The main reactions of the reduction smelting are as follows [4]:

$$FeTiO_3 + C = Fe + TiO_2 + CO \tag{1}$$

$$2FeTiO_3 + 3C = 2Fe + Ti_2O_3 + 3CO \tag{2}$$

$$3FeTiO_3 + 4C = 3Fe + Ti_3O_5 + 4CO \tag{3}$$

$$2FeTiO_3 + C = FeTi_2O_5 + 2Fe + CO \tag{4}$$

$$Fe_2O_3 + C = 2Fe + 3COFe \tag{5}$$

Relatively speaking, the reduction smelting technology is relatively mature technology and suit large scale production, but it has high power consumption than per ton high titanium slag (including TiO_2 72–92%). Power consumption is about

2200–3500 kW-h and 80 kg graphite electrode [5]. Reduction smelting dislodge not iron impurity ability is not remarkably, and can not get high-grade titanium-rich material.

Preparation of Synthetic Rutile by Slag Enrichment

1. Hydrochloric acid direct leaching slag Process

The main component of titanium slag is anosovite which is inert to inorganic acid, so it is difficult to direct product synthetic rutile by using hydrochloric acid in the atmospheric pressure [6]. Using hydrochloric acid pressure leaching, oxidation roasting and reduction of acid leaching, which grade of TiO_2 is higher than normal pressure leaching, but the effect is not obvious, can not meet the production requirements [7].

2. Titanium slag pretreat in high temperature—leaching Process

UGS as a representative of the QIT company, QIT roast the slag which was after reduction smelting in a high temperature (950–1100 °C), then hydrochloric acid pressure leaching in the 150 °C. If the SiO_2 of extraction product content is high, we can reduce the content by alkali leaching. After calcining obtain the titaniferous slag (TiO_2 > 95%) which is called UGS [8]. In spite of the process length and high energy consumption, QIT's use of a large airtight furnace which capacity is 250 kt/a, rich ore resources and cheap power resources is beneficial from the economy of scale.

3. Titanium slag adding additive calcination modification—pickling Process

Many domestic and foreign scholars have done a lot of research on slag modified and make slag structure and phase composition change by adding modifying agent and calcining. The impurity phase of modified titanium slag can easy to remove through chemical method or physical method and obtain high-quality synthetic rutile [9].

Adding alkali metal ion to calcine can improve reaction activity and facilitate reduction effect. Domestic and international's study mainly focus on adding Na_2CO_3 calcining which can destroy the structure and morphology of anosovite in order to speed up the rate of the reaction product of leaching, acid leaching to improve the impurity [1].

The study found that adding suitable amount of iron powder after melting salt activation treatment and leaching with low concentration of hydrochloric acid in the atmospheric pressure activation of high titanium slag can dissolve impurities such as Fe, Si, Al of the titaniferous slag, adjust pH make metatitanic acid precipitation to wash out. The TiO_2 content of synthetic rutile which was prepared by calcining can reach more than 96% [10].

While it is possible to add additives and calcining to obtain a high-grade synthetic rutile, but some additives are expensive and a larger amount of its industrial production needs further study.

Reduction-Rusting Process

The Australian National Institute of Chemistry researched and developed the reduction-rusting process which can make synthetic rutile be produced on a large scale. With the reduction-rusting process, the ferric oxide in ilmenite is reduced to iron, which gathers rust in water to obtain the rich material containing titanium dioxide. Then the material is washed by dilute acid or water, filtrated and dried. Finally the synthetic rutile which is used for produce $TiCl_4$ material can be produced [11]. This synthetic rutile is an excellent source of chloride titanium dioxide production. Domestic and international research on the reduction of corrosion focused on shortening the corrosion time and the most studied is the most obvious effect of corrosion was studied. Becher method using ammonium chloride solution as corrosion liquid and NH_{4+} NH_4^+ is mainly used as a buffer to prevent the "in situ corrosion" occurs [12]. Becher method cannot remove other non-ferrous impurities and the reaction time is long, so it is only suitable for the treatment of high-grade ilmenite slag.

China began to study on the reduction-rusting process technology which is low yields and TiO_2 grade of less than 90% since the early 1970s to product synthetic rutile. Our technology remain has low productivity, long time to rust and corrosion product instability issues [13].

Hydrochloric Acid Leaching

The hydrochloric acid leaching method generally requires different pretreatment according to different ilmenite. The weathered ilmenite sands due to the poor acid-soluble of Fe_2O_3 usually use weak reduction ilmenite to improve the leaching rate and the effect.

American beauty base company is using the circulation of BCA hydrochloric acid leaching method to weak reduction by dilute hydrochloric acid pressure leaching method. Synthetic rutile containing TiO_2 content is 94% was obtained from 54 to 65% TiO_2 titanium iron ore [14].

Hydrochloric acid leaching plays an increasingly important role in the leaching of the metallic iron from the reduction products; the hydrochloric acid is preferred in leaching because it has some advantages, such as fast leaching, remarkable impurity removal and acid regeneration technology that can usefully remove residual iron and other impurities from ilmenite to form synthetic rutile [15].

Carbothermal Reduction-Nitridation

Titanium resources can selectively be chlorinated at temperatures below 200 °C if the TiO_2 in the feed is nitrided before chlorination. Although the SiC can direct chlorination, it can control Si not change to SiC before the nitriding process. Ca, Mg and other impurities are same as TiO_2 which is need a higher temperature to nitride [16]. The mainly reaction of the Carbothermal reduction-nitridation as follow [17]:

$$FeTiO_3 + (4 - x)C + \frac{x}{2}N_2 = TiC_{1-x}N_x + Fe + 3CO$$

X is between 0 and 1.

Ananthapadmanabhan and Taylor [18] synthesized titanium nitride in a thermal plasma reactor from ilmenite ore concentrate using methane and ammonia as the reactive gases. The product has been characterized by X-ray diffraction and SEM and results show that the amount of methane remarkably affects the phase composition of the product.

Welham and Llewellyn [19] synthesized single crystal TiC or TiN powders from ilmenite or TiO_2 within a single low temperature stage. The titaniferous powders were ball milled for 100 h in a laboratory scale with magnesium powder and either graphite or nitrogen as reductant.

In recent years, the scholars has made a lot of attempts and efforts in the preparation of carbo-reduction Ti (C, N) [20], but carbo-reduction process of iron reduction has not been clear enough. The process is not systematic. The pure of Ti (C, N) is not enough, the particle size is too small, or limited production, the subsequent separation of Ti (C, N) and purification of study still blank.

Conclusions

How to utilize the rich reserves of the low grade ilmenite containing high calcium and magnesium in Panxi area to prepare high quality titanium concentrates is the key to promote the development of titanium industry. At present, the methods of preparing titanium-rich materials can not economically and efficiently prepare high-quality titanium-rich materials suitable for chlorination process. Reduction smelting produce titaniferous slag and Reductive leaching produce synthetic rutile method cannot remove the impurities such as calcium and magnesium which must use acid leaching to remove, this not only increased the process and improve the cost, but also bring huge harm to ecology environment. The Acid leaching methods can prepare the suitable for the high quality of rich titanium chloride process, but there is the use of iron is bad and has same environmental problems.

Carbothermal reduction-nitridation of ilmenite can selectively be chlorinated at low temperatures. In the low temperature the impurities such as calcium and magnesium are not molten so can't affect the chloride process, which realize the selective chlorination and reduce the chlorine consumption in chloride process.

In light of the development trend of international titanium materials, the carbothermal reduction-nitridation of ilmenite technology was recommended for possessing Panzhihua natural resource.

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