Present Status and Development of Comprehensive Utilization of Vanadium-Titanium Magnetite

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Abstract There is an abundance of vanadium-titanium magnetite in Panzhihua, China, which contains more than 8.73×10^8 tons of TiO_2 accounting for 90.6% of the national reserves. To fully utilize Panzhihua titanium resources, many processes were proposed. The development and utilization of vanadium-titanium magnetite resource have extremely vital significance. However, its current use of technology is inadequate. This article is a review on techniques to make comprehensive use of vanadium-titanium magnetite, especially in the titanium extraction, and the existing problems are also introduced. The authors predict its possible tendency of development of comprehensive utilization of vanadium-titanium magnetite in the future.

Keywords Utilization of vanadium-titanium magnetite · Panzhihua · Status and development

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Introduction

The main products of vanadium-titanium magnetite beneficiation are titanium iron concentrate (iron ore) containing about 50% of titanium in V-Ti magnetite, ilmenite concentrate containing about 50% of titanium, and cobalt sulfide concentrate [1–4].

Titanium iron concentrate is mainly used for iron making through blast furnace process, which produces a large amount of titanium-containing blast furnace slag with a titanium content of 20%–30 wt%. So far, more than 70 million tons of the titanium-containing blast furnace slag has been produced in Panzhihua and there are no effective ways to make use of it.

Ilmenite concentrate is mainly used to produce titanium-rich materials. Current industrial practices for this purpose mainly include the Electric Smelting Method, the Reduction Roast Method, Choice Chlorination Method, and Acid Leaching Method. However, none of these methods are economically effective for preparation of high quality titanium-rich materials. Impurities such as Ca and Mg, especially those in Panzhihua vanadium-titanium magnetite cannot be removed effectively using the Electric Smelting Method and the Reduction Roast Method. Development of the Choice Chlorination Method is still in a preliminary stage in China while the Acid Leaching Method causes many environmental problems. At present, most titanium white is produced using the traditional sulfuric acid method in China, which generates a lot of "three wastes" (waste gas, waste water and waste residues). With the improvement of the national environmental protection system, it is highly demanded to improve the traditional sulfuric acid method and speed up the industrialization of the Choice Chlorination process.

There is an abundance of vanadium-titanium magnetite in Panzhihua, which contains more than 8.73×10^8 tons of TiO_2 accounting for 90.6% of the national reserves. However, its current use of technology is inadequate. To fully utilize Panzhihua titanium resources, many processes were proposed. The development and utilization of vanadium-titanium magnetite resource have extremely vital significance. This article is a review on techniques to make comprehensive use of vanadium-titanium magnetite, especially on the titanium extraction. Existing problems are also introduced and possible development tendencies are predicted.

Status and Development of Utilization Technique for Titanium Iron Concentrate

The main component of titanium iron concentrate is magnetite. For titanium iron concentrate in Panzhihua, the content of iron is about 50%, and the content of TiO_2 is about 12%. Three process methods, namely the Blast Furnace iron making process, the rotary kiln-electric furnace process, and the reduction-magnetic separation process, dominate the titanium iron concentrate utilization industry in China.

Blast Furnace Iron Making Process

Blast furnace iron making process is one of the earliest methods to utilize titanium iron concentrate. In the process, almost all of the titanium goes into the blast furnace slag, vanadium is reduced into the molten iron. After iron extraction, it produces a large quantity of titanium-containing blast furnace slag with a TiO_2 content of 20%–25 wt%. Over the years, the slag accumulated has reached an enormous amount of 70 million tons. There have been a lot of research focusing on the comprehensive utilization of slag, but none of this research has been successful in developing an effective process. Given the importance of the blast furnace iron making process to the metallurgical industry, it is not very economical and environmentally friendly for the comprehensive utilization of titanium iron concentrate as a substantial amount of titanium is left wasted in the titanium-bearing blast furnace slag which is harmful to the environment [5–8].

Non-blast Furnace Iron Making Process

The method of extracting vanadium and titanium from titanium iron concentrate is referred to as the non-blast furnace iron making process, such as electric furnace smelting process and reduction-grinding separation process. Electric furnace smelting process is a method of separation of titanium and iron by electric furnace. It is principally similar to the blast furnace iron making process but is simpler in operation. Nevertheless, it's not as widely used because of the (high) viscosity of titanium slag. In reduction-grinding separation process, the ferriferous oxides are reduced in solid phase by the reductant of coal firstly, but the titanium remains oxide, then ferrous micro-bead is separated from the products by magnetic separation. Although titanium and iron can be separated from titanium iron concentrate in solid state in the reduction-magnetic separation process without formation of foaming slag, high requirement of iron particles in the (subsequent) reduction process constitutes a major restraint to the wide application of the non-blast furnace iron making process [9, 10].

Status and Development of Utilization Technique on Ilmenite Concentrate

Ilmenite concentrate with TiO_2 grade of about 45% is the main raw material for preparation of titanium dioxide and sponge titanium. As the Ti content in the titanium concentrate is not high enough for production of Ti or Ti alloy, further enrichment is desired to transform the titanium concentrate into high titanium-containing slag and rutile. The enrichment treatment can also reduce the production cost of the final product. There are many concentration methods, three of which will be review as below.

Electric Smelting Method

Putting ilmenite concentrate and coke in electric arc furnace and smelting at temperature above 1350 °C, ferriferous oxides are reduced to liquid iron settling in the furnace, and TiO_2 is enriched in the slag floating on liquid iron meanwhile. Impurities cannot be removed perfectly with this method. The content of inorganic impurities in ilmenite concentrate, especially non-ferrous impurities, has an important influence on titanium slag grade. The titanium slag grade prepared from Panzhihua titanium concentrate through the electric furnace smelting method is not very high ($\sim$wt 75%) due to the presence of alkaline earth metal oxides in the titanium concentrate, e.g., MgO, CaO, and Al_2O_3. Further enrichment processes are essential to prepare high titanium slag, but these processes, e.g., the sulfuric acid process, may have a bad impact on the environment. The Electric Smelting method features less pollutants generated and simple operation and it is suitable for hydropower rich areas [11].

Choice Chlorination Method

Different substances in ilmenite concentrate have different thermodynamic qualities. Under certain condition (temperature at about 900–1100 °C), iron oxides will react with Cl_2 to form $FeCl_3$ which can be removed easily. The process has the advantages of simple process, easy production and low power consumption. However, the process is difficult to solve the problems caused by impurities such as $MgCl_2$ and $CaCl_2$, and the corrosion problems caused by chlorine and hydrogen chloride as well [11].

Reduction Process

Researches on reduction process are relatively early. Most of the processes are carbon reduction methods wherein titanium concentrate mixed with carbon powder is reduced. Product of the reaction in air is a solid solution of TiC and TiNO. Using the reduction product as raw material, $TiCl_4$ can be synthesized through chlorination. The main problem of this method is that the reduction temperature is high and the production capacity is low.

There are many wet metallurgical utilization methods to enrich titanium, such as acid Leaching Method, reduction-hydrochloric acid solution, etc. These methods have common disadvantages: difficulties in dealing with acid leaching waste and iron products, inefficiencies, and serious corrosion of equipment [12, 13].

Status and Development of Utilization Technique on Titanium-Bearing Blast Furnace Slag

Almost all of titanium iron concentrates use in blast furnace and most of TiO_2 go into blast furnace slag. Iron concentrate used in blast furnace iron making process has produced almost 70 million tons titanium-containing blast furnace slag with TiO_2 content of 20%–25 wt% in Panzhihua. Comprehensive utilization of titanium-bearing blast furnace slag has great practical significance. Many scholars at home and abroad have done a great deal of researches on the slag.

Technique on Non-Titanium Extraction

Techniques on non-titanium extraction are mainly found in the following applications: cement admixture or concrete aggregate; materials of sanitary porcelain, glazed tiles, ceramic tiles or floor tiles; preparation of cast stone, alkali resistant glass fiber or mineral wool. It is a great waste of titanium resources that titanium in the slag is not effectively used with these techniques. The blast furnace slag is directly used for the production of building materials and other products without extracting valuable elements in it. These processes are poor in economic efficiency, and their products are of low relative added values. Along with the development of titanium and its alloy industry, comprehensive utilization of titanium in blast furnace slag has become the consensus of researchers. Non-Titanium extraction technologies have been gradually phased out [1, 14].

Technique on Titanium Extraction

The blast furnace slag in Panzhihua is an important titanium resource, which contains rich titanium and can be exploited comprehensively. Universities and scientific research institutions at home and abroad have conducted a lot of researches on titanium extraction from the slag.

1. Preparation of TiO_2 by sulfuric acid leaching of Titanium-bearing Blast Furnace Slag: This method produces titanium white from blast furnace slag with sulfuric acid leaching, hydrolyzing, extraction and precipitating separation. To produce a single ton of TiO_2, it takes about 6 tons of concentrated sulfuric acid, etc. The recovery rate of the Titanium is up to 73.4%, but this process consumes large

amounts of sulfuric acid and produces a large number of residual acid leaching liquid and dregs which are difficult to use and cause environment pollution. In addition, the production efficiency of the process is not high [15].

2. Preparation of Ti-Si-Al alloy: The process produces Ti-Si-Al alloy from blast furnace slag by reduction with 75% ferrosilicon (lime as a flux). The purity of product in this process is not high, and there is still a lot of residual titanium remaining in slag. The cost of this process is relatively high as well [16].
3. Alkali-Treatment Process: This method is to separate titanium from the slag by NaOH. The consumption of alkali in this process is large (one ton of slag using about 200–250 kg of NaOH). If considering the problem of sodium salt recovery, the process would be further complicated and costs would be greatly increased. Moreover, the enrichment of titanium is not good, and alkali treatment of blast furnace slag at high temperature will produce more serious air pollution [17].
4. Selective Enrichment of perovskite from Titanium-bearing Blast Furnace Slag: This process makes titanium components dispersed in the slag transfer and concentrate in the designed mineral phase-perovskite phase, and separates perovskite phase from the modified slags by beneficiation. The advantages of this process are low environmental pollution, low cost and high processing capacity. The perovskite is of different and non-uniform size, and accretes with spinel. This above feature makes the valuable single mineral-perovskite difficult to liberate [18, 19].
5. High-temperature Carbonization and Low-temperature Chlorination: TiC is prepared by the carbon thermal reduction method from the slag at high temperature (1600–1700 °C) and distributed diffusely in products. After crushing and magnetic separation, TiC will be enriched in slag. Then, the slag containing TiC can produce $TiCl_4$ by reaction of chlorination at low temperature. It is very difficult to dissociate and enrich TiC from products. Serious corrosion of equipment occurs and a large number of dilute hydrochloric acid is produced in chlorination process [1, 20].

Status and Development of Utilization Technique on High Titanium Slag

The grades of Ti-rich material from ilmenite concentrate in Panzhihua are around 75% because of lots of alkaline earth metal oxides such as MgO, CaO and Al_2O_3 contained in ilmenite concentrate. The Ti-rich material is only suitable for production of titanium dioxide as a raw material in sulfuric acid leaching process instead of chlorinating process. To prevent serious environmental problems created by sulfuric acid method, Ti-rich material needs to be further enriched to high titanium slag with grades higher than 90 wt% which is suitable for preparation of pigment and sponge titanium [1, 19].

Conclusion

Based on the introduction and analysis of these technologies on comprehensive utilization of vanadium-titanium magnetite in Panzhihua, all of these technologies are restricted by the problems of technology advantages, industrialization, energy saving, environmental protection, etc. The abundant situation of titanium mineral resources in Panzhihua is not commensurate with titanium industry and preparation technology.

So far, in Panzhihua, the titanium iron concentrate is mainly used in blast furnace to produce vanadium-bearing hot metal, and the ilmenite concentrate is mainly used in electric arc furnace to produce titanium slag, and the blast furnace slag is lack of the rational industrial scheme to recovery titanium.

Vanadium and titanium iron concentrate is one kind of iron, vanadium, titanium multiple-element symbiotic composite ore, which has extremely high comprehensive utilization value. Practice on the development and utilization of vanadium-titanium magnetite resources in Panzhihua is very significant. Although a great deal of research has been done, comprehensive utilization technique on vanadium-titanium magnetite has not been able to make a breakthrough progress.

Efficient preconcentration and extraction of titanium from titanium bearing blast furnace slag, titanium concentrate, rich titanium material or high titanium slag, and changing iron making process for the main method of utilization of titanium iron concentrate are the focuses and also challenges in the research and development of comprehensive utilization of vanadium-titanium magnetite. With the social development in recent years, the energy and environmental problems get more and more concerned, extracting hydrogen from coke oven gas in BF iron making processes and preparing Ti-rich material or synthetic rut by Hydrogenous Reduction will be probably a good approach.

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