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Resources Recycling of a Special Blast Furnace Slag-Bearing TiO_2

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In this paper the forming and the unique properties of PZH blast furnace slag, bearing TiO_2 22~25%, have been introduced. The utilization of this kind of blast furnace slag, especially about recycling resource of TiO_2 included in it, has been reviewed and discussed. According to research work experiences and tendency of new materials developing some suggestions about future research on PZH blast furnace slag have been put forward.
Keywords: blast furnace slag, titanium slag, comprehensive utilization, environment protection

Introduction

There is a special kind of magnetite whose Fe content is about 26~33%, TiO_2 6~12% and V_2O_5 0.2~0.3% in Pan Zhi Hua---Xi Chang area in southwest of China[1]. The 29.6% percent of worldwide V & Ti magnetite reserves come from here. Now the Fe and V resource in it has been successfully utilized after several decade year research works. But the utilization of Ti resource is still a problem. Because the titanium and iron accrete compactly, it is hard to separate titanium from iron by mechanical way in grinding and concentrating processing. So titanium existed in ore goes into BF (blast furnace) with iron. During smelting in BF some of TiO_2 in sinter will be reduced to lower valence compounds such as Ti_2O_3, TiO, TiC, TiN and their fusion. But most of them could not be reduced. They combine chemically with another major content in sinter---CaO to form perovskite that is a main phase in BF slag. The reason for that is although generally the TiO_2 is considered as an amphoteric oxide it actually shows acidity when it is in the BF slag[2]. That results in reducing the superfluous alkalinity of the BF slag and making against desulfurazition. In order to ensure the fluidity and desulfurazition ability of the slag, the alkalinity of the slag is increased result in promoting CaO and TiO_2 reacting and reduce the activity of the TiO_2. Therefore the titanium in sintering ore almost enter into BF slag[1], which make the slag produced from iron-making in BF containing TiO_2 about 22~25%. Every year this kind of slag produced in Pangang (Pan Zhi Hua Iron and Steel (group) Company) almost reached 2.5 million tons. It means about 0.5 million TiO_2 that could not be recycled. Now we realized that it is a very important secondary titanium resource.

The blast furnace slag bearing TiO_2 is different from the normal slag because its TiO_2 content is higher. For example, its melting temperature is high, mineral lithofacies is steady, superfluous alkalinity is low and it is hard and has no or little chemical activity and so on. So that slag can not be largely used as the raw material for Portland cement as normal BF slag. In addition TiO_2 is a useful material for chemical industry. It can be processed as titanium white powder that is used in widely scope. But an effective way to recycle it comprehensively has been not found yet up to now.

Recycling Research Work

The research work of recycling BF slag bearing TiO_2 was started in 1960s. And research efforts are continuing till now. Although many ways of recycling it have been developed they still have some problems, such as cost is high and pollution of environment, which prevent putting them into practice. The research emphasis of recycling the BF slag bearing high TiO_2 should be finding a way not only extracting titanium and largely using residua but also be feasible in the point of view of technology and economics.

Previous research work

The previous research work was developed from two directions. One is utilizing the BF slag without extracting TiO_2 from it. The other is using slag through extracting TiO_2 from it.

Utilizing Without Extraction TiO_2

In 1970s, the research of using BF slag bearing TiO_2 to make crystallitic cast stone or cast tone tube was developed. Comparing with normal cast stone (tube), it has better

thermal stability and ability to resist strike, chemical erode and wearing[3]. So it can replace cast iron, steel and rubber as the lining of some equipment. In 1980s, the investigation of utilizing the slag to produce ceramic tile was conducted. This technique can save energy because it makes use of potential caloric of melting slag. But the test was done only in lab. After that Pangang academe and Ren He ceramic factory commonly investigate to manufacture vitreous enamel brick using Pangang BF slag bearing TiO_2. The result shows that the vitreous enamel brick produced from mixture of BF slag bearing TiO_2 and local china clay can meet the national standard. And it has the virtues of lower sintering temperature, saving energy and prolonging the using life of furnace comparing with traditional techniques.

Utilizing through extraction Ti resource

Chongqing University of China did some experiments of smelting Si-Ti alloy using Pangang BF slag bearing TiO_2 in 1968[4]. The material is BF slag whose TiO_2 content is 30%. The rate of Si-Fe to the BF slag is 44.6:100. The average titanium content of Si-Ti alloy is 19.56%. The experiment proves that Si-Ti alloy cannot only take the place of Ti-Fe but also save the usage amount of Si-Fe. That means 1kg Si-Fe, silicon content is 75%, can be reduced for producing per ton steel. The research of melting Pangang BF slag to produce Si-Ti-Al alloy was also done. The BF slag and Al_2O_3 is melted together to make Si-Ti-Al alloy in aluminum electrobath. The titanium content of the alloy can reach to 1.0~1.5%. And the rate of recycling titanium in the slag can arrive at 66.17%[3].

Of course, there is research of using the BF slag bearing TiO_2 as the material such as making rutile. The methods include boiling chlorination, vitrol method, hydrochloric acid method, oxidizing method and so on. But all these method exist a problem of the slag's TiO_2 content being low. That results in increasing the cost and polluting the environment.

Present work

Study on crystallization behavior

Wang Xidong[5] carried out the study on crystallization behavior of blast furnace slag bearing TiO_2. The effect of SiO_2 and TiO_2 on crystallization behavior of CaO-SiO_2-TiO_2- MgO-Al_2O_3 slag systems studied through differential thermal analysis and optical microscope. The mineral crystalline region of perovskite and anosovite is determined in phase diagram. The study provided a theoretical basis for reducing TiO_2 content in BF slag bearing TiO_2 by crystallization extraction method and for the comprehensive utilization of the slag.

Phase separation

Recently Sun Kang[6], from Northeast University of China has investigated to synthetically utilize Pangang BF slag by separating phase with two steps. Firstly the phase separation method is adopted to separate the titanium and the most silicon from the slag at a higher temperature. Then the phase separation method is re-adopted to separate titanium from silicon at room temperature. According to thermodynamic analysis and experimental determination, the main products of reaction between the slag and Na_2CO_3 at high temperature were complex silicon and titanium oxides containing sodium. But the forming rule and transforming degree are not made clear.

Separation Titania

Zhou et al[7] put forward the test of separation titania from blast furnace slag bearing high titania. Alkaline separation agents were added into slag bearing high titania. Structure of perovskite in the slag is destroyed at the high temperature and co-molten slag formed is leached in water. The tests indicate that the interaction of slag and separation agents belongs in the acid-base reaction at optimum temperature ranges of 1200~1300℃ and TiO_2 content in the slag is reduced to a certain degree after leaching.

Separating Perovskite

Bai et al[8] has work out that TiO_2 containing in the perovskite is occupied 74~85% of all TiO_2 in slag. Therefore it is thought that the titania amount of the Pangang BF slag can be reduced largely through separating perovskite from the slag. The titania content of perovskite is richer than other minerals of the slag. Then it might be used as the material for making rutile, white titanium powder and melting Ti-Fe alloy. The residua can be used as the material of cement as normal slag. Therefore some researches are developed.

Quan Yao et al[9] put forward the research of floatation perovskite from the BF slag bearing titania. And Bai et al[8] investigated separation perovskite from the BF slag bearing high titania with magnetic force. Both separate effects are not satisfactory. The results show that perovskite can be separated from the slag if the grain size of it exceed 40μm. But the distribution of the perovskite in the slag has the character of fine and disperse. And the grain size of the slag is about 71μm even it is ground to 200 mesh. That can not met the demand of floatation separation. The problem can be resolved from two ways. One is promoting perovskite to grow and enrich. The other is grinding the slag more finely.

Sui Zhitong et al[10] investigated the precipitating behavior of perovskite phase in the BF slag bearing higher titania. The precipitating behavior of perovskite phase in isothermal and continuous cooling processes was investigated in order to promote the selective precipitation of perovskite phase in the slag and to meet the requirement for separation process. The experimental results showed that the suitable temperature range for precipitating perovskite phase was from 1300℃ to 1400℃ in which the precipitation was promoted effectively and its dendrites were coarsened by cooling the molten slag slowly (cooling rate 0.5℃/min). As a result, the precipitating rate was 24.89% and the grain size 48.27μm. In addition, the coarsing mechanism of perovskite phase was discussed by studying its morphology changes. The effects of chemical composition on the precipitaion quantity and crystal morphology of perovskite in high titanium blast furnace slag were studied. The results showed that the precipitating quantity of the perovskite was increased and its crystal morphology was transformed from fine dendrite crystals into coarsened equal axes ones with increasing the alkalinity of the slag. It will be providing necessary conditions for further separating perovskite from slag.

Microwave Processing

As for grinding, the BF slag bearing titania is hard to be crushed. Moreover the efficiency of traditional way is relatively low. So the energy consumed to comminuted the slag to 40μm will be enormous. The alternatives have to be searched for comminuting the slag in the point of view of economic benefit. An alternative way of heating emerged recently is microwave heating. It also have the ability of utilizing tension to break mineral. That will improve the efficiency of grinding because the tensile strength may be as little as one tenth of the compressive strength of the mineral. Microwave energy can be used to induce thermal stress cracking to decrease the energy requirements of grinding mineral.

On the count of that, Bai[11] considered a way of pretreatment the BF slag bearing titania with microwave. Through experiment to observe the effect of microwave on the precipitating of perovskite and that if any cracks would be appeared in the crystal board between perovskite and other phase. Four different kinds of BF slag samples, which have different TiO_2 content, have been tested. Sample 1 is that has 22% TiO_2 and cooled in natural condition. Sample 2 with 13% TiO_2 quenched in water. Sample 3 and sample 4 have the same TiO_2 content as sample 1 but water quenching. It is shown from figure 1 that general PZH BF slag (sample 1) could be heated rapidly by microwave. In

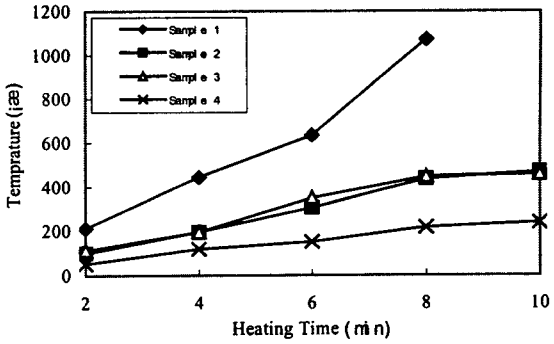


Fig.1 Effect of microwave on slag samples

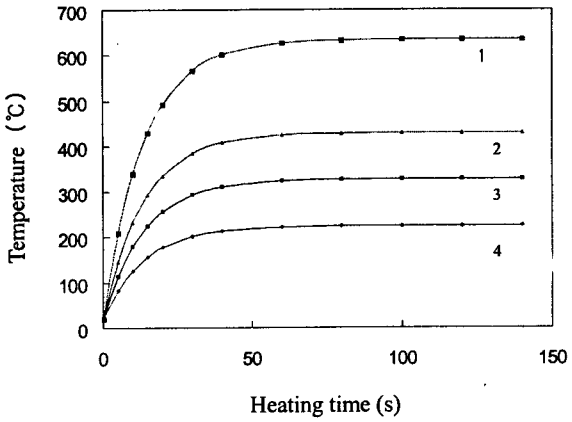
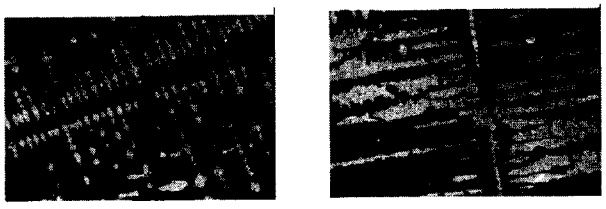


Fig 2 The effect of microwave power on the temperature rising rate of BF slag

1. 1500W 2. 1000W 3. 750W 4. 500W

ten minute the temperature of 120g sample raised over 1200 ℃ (the input power of the microwave oven is 750W). In the same time other samples could not be over 500℃. Beside heating experiment the preliminary results also include optical microscope observision from which it could be seen that recrystallization occurred in the slag with microwave heating. From Fig.3 it can be seen the pricipitating rate and



(a) ×100 (b) ×100

Fig.3 Comparing of slag sample before (a) and after (b) microwave processing

the grain size of perovskite are increasted with the heating time. Unfortunately the cracks between perovskite and other minerals have not been observed. Perhaps because of the tension force not higher enough. Through methmatical model it can be calculated that the temperature and the rate

of temperature rising of the slag will increased with increasement of the input power of the microwave (Fig 2). As a result, the tension force in the slag will increase. As far as how much input power required to induce the crack between the perovskite and other minerals can not be calcullated exactlly because of lack of the date about the dielectric and tension of the BF slag bearing TiO_2. So there many research work for us to study further.

Future

The research of the structure and the performance of normal slag have been furthered and forming a subject, the blast furnace chemistry. However, the investigation of the structure and performance of the BF slag bearing TiO_2 is less. And the study is not systemic enough. Therefore, the author suggests to conduct the research of the structure and performance of the BF slag bearing TiO_2 applying some high technology way. On the base of making clear the structure of the BF slag bearing TiO_2, it is possible to find a feasible way of utilization the BF slag bearing TiO_2 comprehensively.

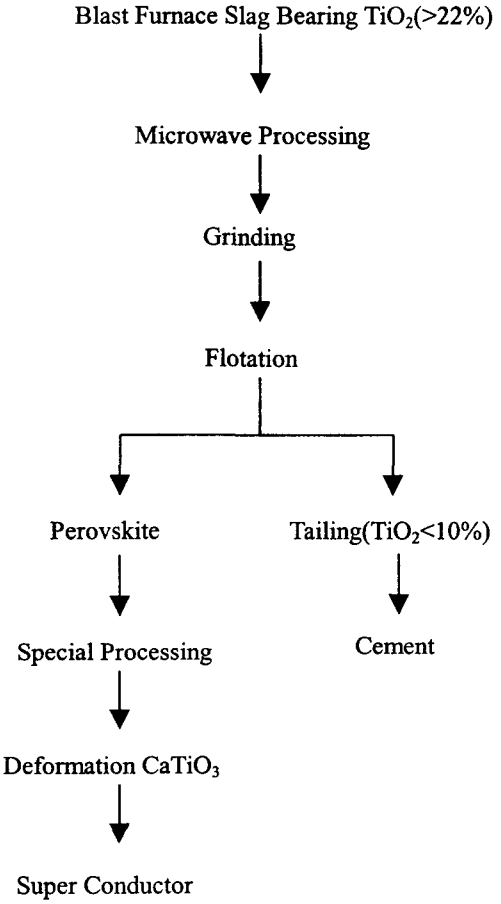
Direct Using

In this category the slag used as the raw materials for certain product, for example, for Portland cement, constructing industrial ceramics, ceramic tile, protection hearth lining materials and so on. In summary there is no necessary of pretreatment for slag before using. So the advantage of that sort is technology relatively simple. But there are some disadvantages exist. First the titania hold in the slag could not be extracted and used. This is uneconomic in the point of view of the resource sufficiently utilization. Secondly the blast furnace slag bearing TiO_2 is some quite harder because of the perovskite i.e. TiO_2 existing. Thirdly all the technologies mentioned above consume the slag not so much. So the key point is how to separate perovskite from the slag.

Comprehension Using

In this sort the basic idea is that extracting TiO_2 from slag and then using the balance in the elsewhere. Unfortunately TiO_2 abstracting from slag is very difficulty because of economic and technique problems. There are other two ways: one is production of Si-Ti alloy with slag by electric furnace to avoid the waste of Ti. The other is that slag would be carbonized deeply in order that titanium oxide in slag could be reduced by carbon and produced TiC. Until now the same problems as mentioned above is still existed.

It seems that extracting perovskite from the BF slag bearing high TiO_2 is feasible. Economically the extracted perovskite can be produced to high added value products, or at least some raw materials, with minerals bearing TiO_2. The balance of the slag can be used for cement. Technologically it is known from primary research that the grain size of perovskite will increase when pretreatment of the precipitating condition. A way may be found to meet the demand for flotation perovskite from the slag. It is necessary for us to study the precipitating of perovskite in the BF slag bearing TiO_2 especially when it is heated with microwave. The author bring out new idea for solving problem as follows:



Conclusion

From above analysis and discussion the fallowing conclusion can be obtained.

1. The BF slag produced in PZH iron & Steel (Group) Company is a very important recycling resource of TiO_2. Every year about 0.5 million ton of TiO_2 is waste if we cannot find a way to use it.
2. Many efforts have been made to solving this problem, but a real way that can be used to deal with it has not been

found yet.

3. The new technology should be utilized to research of the structure and performance of the BF slag bearing TiO_2 in order to find a feasible way of utilization it comprehensively.

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