PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in or relating to the Treatment of Ferro-titaniferous Materials

We, TITAN COMPANY INC., a Corporation organized and existing under the laws of the State of Delaware, United States of America, of Wilmington, Delaware, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention is for improvements in or relating to the treatment of ferro-titaniferous materials. More particularly, it relates to a process for removing iron from titaniferous materials and for the preparation of titanium oxide concentrates.

The principal raw material containing titanium compounds is ilmenite of which several different types are known. Ilmenite occurs in many rocks and sands and this mineral is considered to consist mainly of iron titanates of different composition. Most ilmenite concentrates on the market contain usually between 30% and 60% TiO_2 and have undergone a mechanical ore dressing operation including wet separation of gangue and magnetic separation of minerals more or less magnetic than ilmenite.

Ilmenite concentrates obtained by mechanical operation often show the highest TiO_2 content which can be practically reached without resorting to chemical or metallurgical treatment. As, however, the iron content of the commercial ilmenites is rather high, usually between 25% and 40% of Fe, of the total content, or between 40% and 80% of Fe calculated on the TiO_2 content, it will be realised that removal of a considerable part of the iron in an economical manner is a problem of importance.

Several methods for extraction of iron from ferrotitaniferous ores have been proposed as, for instance, methods consisting in treatment of ilmenite with strong acids or alkalies, but these methods are not considered to be economical in the production of TiO_2 concentrates for industrial purposes.

[*Price* 1/-]

It has also been proposed to heat ferro-titanium ores in an oxidising or a reducing atmosphere whereby the ores are rendered more adaptable to a subsequent extraction of the iron with dilute acids or solutions of salts or of other reactive agents; however, these processes have attained no technical importance because of the comparatively high expenses involved in the consumption of the required chemicals and also because of the complicated equipment required for such operations.

It has further been proposed to treat ferro-titanium ores by a thermal reduction process with a subsequent mechanical separation of the metallic iron and the titaniferous material.

The object of the present invention is to remove iron from ferro-titaniferous ores in a much simpler way, involving less expenses, than hitherto known. In accordance with the present invention, there is provided a process of treating ferro-titaniferous materials to increase the titanium concentration thereof, which comprises reducing iron compounds therein to the metallic state, converting the metallic iron into oxides, and removing resulting iron-oxygen compounds from the residual titanium concentrate.

A preferred feature of this invention comprises thermal reduction of a ferro-titaniferous ore whereby iron therein is converted into a finely-divided metallic state, oxidation of that metallic iron to form hydrated oxide compounds and removal of such oxide compounds from the residual titanium concentrate.

In carrying out the process of the invention in practice, it may be divided into the following steps:

a) Thermal reduction of the material or ore under conditions which convert iron into metallic state in a finely divided form;

b) Conversion of the metallic iron into oxide compounds by a suitable oxidising treatment, preferably by action of air in the presence of water or steam or both; and

c) Removal of the iron oxide com-

pounds from the other components by washing, magnetic treatment or in other ways.

The thermal reduction may be carried out in such a way that the ferro-titanium ore, for instance in form of ilmenite concentrate, is heated to 700°—1100° C. in a reducing atmosphere. If gases such as hydrogen, carbon monoxide, coal gas or water gas, are used as reducing agents, the reduction proceeds fairly well at 700°—900° C. If solid reducing agents are used, the crushed ferro-titanium ore is mixed with the reducing agent and the mixture is heated to a temperature somewhat higher than when gaseous reduction is applied, the preferred temperature being dependent upon the working conditions and the quality of the ore.

When using solid reducing agents, enough should preferably be used so that a surplus is left in the finished reduced product. Reduction in stationary retorts requires generally a larger surplus of reducing agent than reduction in rotary kilns.

The discharge from the reduction retort or kiln should be cooled under such conditions that re-oxidation is avoided and the reduced material should not undergo changes which render it less reactive during the subsequent oxidation process. A quick cooling process is preferred.

The reduced material may be stored for months without losing its reactivity when it is kept under dry conditions.

The extent to which the iron content should be reduced to the metallic state, is dependent upon the quantity of iron oxides which is to be removed. In many cases it is sufficient to reduce only one half of the total iron contained in the ore and a considerable increase of the titanium content may be obtained even by removal of less of this iron. In order to get a concentrate exceptionally rich in TiO_2 containing, for instance, 75—85% TiO_2, most of the iron should be reduced but it is seldom necessary to reduce more than 90—95% of the total iron, and this facilitates the reduction process to a great extent.

The oxidation of the metallic iron is preferably carried out by the action of air in combination with water or steam or both under controlled conditions. The temperature of the charge is easily regulated by adjusting the quantities of air, water and steam introduced.

Addition of water should be made in such a way that the whole mass is thoroughly wetted but without introduction of surplus water beyond this point. Air (or other oxidising gases) should be in contact with the mass but the oxidation should not be so intense that a water-poor ferric oxide (Fe_2O_3) or rusty products are formed which are difficult to separate from the titaniferous material by a simple washing operation, or a magnetic treatment.

The exact composition of the iron oxides which are more or less hydrated is not quite clear, but their appearance and consistency are characteristic, and it is easy to control the oxidation operation so as to obtain products with the desired properties. Generally, the colour of the iron oxides should be dark, similar to Fe_3O_4 with no noteworthy traces of red or yellow iron hydrates. During the oxidation the volume of the mass increases, whereby the mass becomes looser and acquires an appearance similar to moist dark earth.

If the oxidation is carried out under too dry conditions or at too high temperatures, a film of oxidised iron may be formed on the surface of the metallic iron and retard the oxidation process. Sometimes, it is preferred to interrupt the oxidation before all of the iron is oxidised, thus obtaining a product wherein for example, at least 95% of the metallic iron has been oxidised and the remainder of the iron is in the metallic state.

Experiments have proved that the oxidation of the iron may be considerably accelerated by using additions of electrolytes, such as NaCl, $MgCl_2$, $Ca(NO_3)_2$, HCl and HNO_3. Also, the presence of CO_2 or CO_2-containing gases accelerates the oxidation of the metallic iron to a considerable extent. It should be understood that other oxidising agents may be used alone or in combination with air. Thus acids and salts developing oxygen may be used, for instance, nitric acid, nitrates, chlorates and perchlorates.

When the oxidation is carried out in steps, it has in many cases proved an advantage to use air in one or more of these steps and acids or salts developing oxygen in the subsequent steps.

Furthermore, the temperature has proved to be of great importance in the oxidation operation. For some of the reduced ilmenites, the oxidation proceeds rapidly at 60°—80° C. but even as low a temperature as 20° may be sufficient to maintain the oxidation. A temperature of above 100° C. may also be used as it has been found that water or steam introduced into the charge at such high temperature is partially absorbed by the material, giving hydrated iron oxides and accelerating the oxidation. Generally, temperatures of above 200° C. will

not allow sufficient water to combine with the iron oxides and will result in iron oxides which are dry and hard and make the separation of these oxides by washing difficult. Temperatures above 200° C. will, therefore, only be used in exceptional cases. In any case, the temperature should be kept below about 750° C. in order to prevent a re-combination of iron and titanium oxides.

Experiments have shown that the heat of oxidation may be utilised advantageously in the oxidation process.

It has been found that, during the oxidation, it is not necessary to keep the mass in motion, but moving the mass either occasionally or continuously will accelerate the oxidation process. The oxidation may, as already stated, be carried out in one or more steps dependent upon the material and the apparatus used.

When the oxidation operation has reached the desired degree, the iron oxides produced may be separated from the titanium concentrate by subjecting the charge to strong agitation in presence of water or by some sort of motion which causes the particles to rub or grind against each other. This operation may be carried out in rotary drums, ore classifiers or other suitable apparatus. After such operation, the iron oxides are easily suspended in water and separated from the titanium concentrate by washing and decantation. The iron oxides in suspension will readily settle when left in settling tanks, and can then be filtered and dried. They form a soft, finely divided, uniform product valuable as raw material in the production of iron oxide pigments and other iron compounds. The product is also of value in the production of iron, steel and ferro-alloys. Analysis of the iron oxides has shown 65%—70% Fe dependent upon the temperature of drying or roasting.

The titanium concentrate may be washed, dried or calcined and makes an excellent material for the production of titanium compounds, for metallurgical purposes as well as for the production of titanium pigments.

In order to illustrate the invention the following, non-limitative examples are given:

EXAMPLE I.

1,000 kilograms of ilmenite concentrate containing 44% TiO_2 and 36% Fe and having a grain size of about 1/2 mm. size, were mixed with 300 kilograms of charcoal and heated in a rotary kiln to 950° C. and kept at this temperature for 1 hour, after which time about 90% of the total iron content had been converted to metallic state. The reduced material was cooled without access of air to about 300° C. and thereafter quenched in water. The surplus of coal was washed away, advantage being taken of the great difference in specific gravity and settling between ore and coal, and the reduced material was de-watered on a rotary filter.

The moist material was then placed in a rotary drum and a small amount of a weak solution of magnesium chloride added. The drum was kept in a slow rotation, and water and steam were introduced under controlled conditions so that the charge was kept within the temperature range of 50—80° C. In the course of about 6 hours the content of metallic iron had been reduced from 36% to 5%, iron oxides having been formed in corresponding quantities. More water was then introduced and the speed of rotation increased, thereby submitting the charge to strong agitation in water. After about 1 hour the iron oxides were in suspension and were removed by decantation and washing. The titanium concentrate was de-watered on a filter and dried. Analysis of the treated material showed that the content of TiO_2 had increased from 44% in the original material to 68% in the finished product, and that the total content of iron had decreased from 36% in the original material to about 16% in the finished product.

EXAMPLE II.

A titano-magnetite which contained about 20% TiO_2, was reduced with hydrogen at 870° C. until about 90% of the iron content had been converted into finely divided metallic iron. The reduced material was quenched in water and dewatered on a filter, whereafter it was treated in the same way as described in Example I. The oxidation took place in stationary troughs with occasional stirring of the charge.

After removal of the iron oxides by washing, a concentrate was obtained, containing 40% TiO_2.

While ilmenite is the principal raw material in the production of titanium compounds at the present time, many other ferro-titaniferous ores may be suitable. Due to the high iron content, however, they have not found commercial application. The present invention permits the removal of iron in a simple and economical manner and will therefore be of value in the application of such ores. The invention is therefore not limited to high class ferro-titaniferous ores like ilmenite concentrates, but also may be applied ferro-titaniferous ores which are considered to be of less value, if any,

at the present time.

In some types of ferro-titaniferous materials it is difficult under commercial conditions to reduce more than 90% of the iron into the metallic state in one operation. In such cases, practically the total amount of iron may be reduced by effecting the reduction operation in two successive steps. Ferro-titaniferous materials in which the iron is present in the form of iron silicates or of similar compounds and which make reduction to the finely divided metallic state difficult, may be subjected to preliminary magnetic treatment, electroflotation or air separation in order to separate out such minerals.

After reduction, the surplus of solid reducing material in the charge is removed by washing and is then recovered by filtration.

By washing the charge in a rotating drum in the presence of an excess of water, the iron oxides formed are suspended and easily separated by decantation, settling and filtration. In this way, the surface of the metallic iron becomes free and the oxidation of the remaining iron may continue.

It is obvious that the process may be interrupted at any time desired and that titanium concentrates with different content of TiO_2 may be obtained.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process of treating ferro-titaniferous materials to increase the titanium concentration thereof, which comprises reducing iron compounds therein to the metallic state, converting the metallic iron into oxides, and removing resulting iron-oxygen compounds from the residual titanium concentrate.

2. A process of treating ferro-titaniferous materials to increase the titanium concentration thereof, which comprises thermally reducing iron compounds therein to the metallic state, oxidising the metallic iron by means of atmospheric oxygen, and removing resulting iron-oxygen compounds from the residual titanium concentrate.

3. A process as claimed in claim 1 or claim 2 wherein the step of oxidising the metallic iron results in a hydrated oxide product.

4. A process according to claim 1 or claim 2, in which the reduction is effected under conditions which produce finely divided metallic iron.

5. A process according to any one of claims 1 to 4 in which the oxidation is effected in the presence of water and/or steam.

6. A process according to any one of the preceding claims in which the reaction conditions during oxidation are controlled by a regulated introduction of water, air and steam.

7. A process according to any of claims 1 to 6, in which the oxidation is effected in the presence of an oxidation-accelerating catalyst.

8. A process according to any of claims 1 to 7, in which the oxidation is effected at temperatures below about 750° C. and preferably below 200° C.

9. A process according to any of claims 1 to 8, in which the iron-oxygen compounds are mechanically removed.

10. A process according to any of claims 1 to 8, in which the iron-oxygen compounds are removed by agitating the treated material in water and separating the suspended iron-oxygen compounds.

11. A process according to any of claims 1 to 8, in which the iron-oxygen compounds are removed by electroflotation.

12. A process according to any of claims 1 to 8, in which the iron-oxygen compounds are removed by wet flotation.

13. A process according to any of claims 1 to 8, in which the iron-oxygen compounds are removed by air flotation.

14. A process of treating ferro-titaniferous materials to increase the titanium concentration thereof as claimed in claim 1 or claim 2 and substantially as hereinbefore described.

15. A titanium concentrate whenever prepared by the process claimed in any one of the preceding claims.

16. A titanium concentrate according to claim 15 containing above 65% TiO_2 and less than 5% metallic iron.

17. Iron-oxygen compounds whenever prepared by the process hereinbefore claimed.

Dated this 14th day of March, 1941.
BOULT, WADE & TENNANT,
111 & 112, Hatton Garden,
London, E.C.1,
Chartered Patent Agents.

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Steven Lorgren Perry . Rollin

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