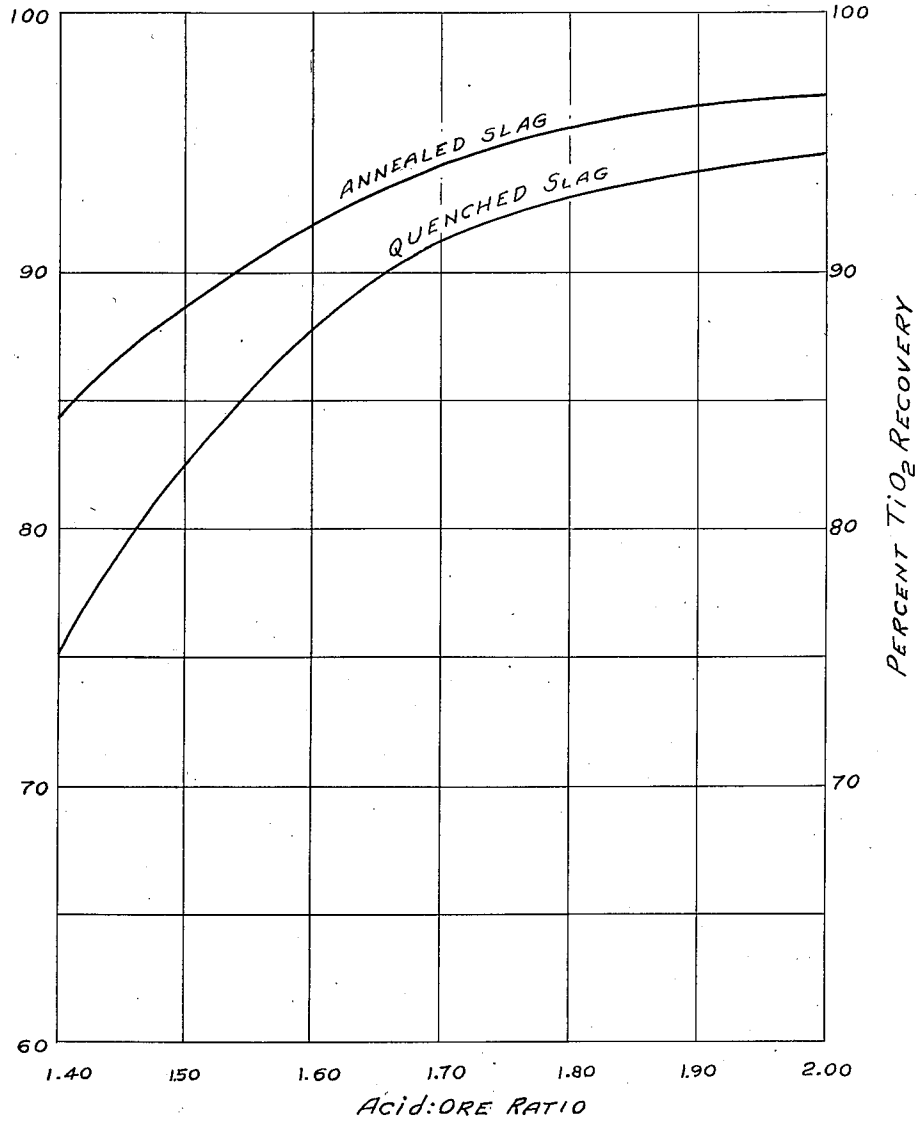
July 2, 1957 R. J. MAGRI, JR., ET AL 2,798,048

ANNEALED TITANIUM-BEARING SLAGS OF IMPROVED REACTIVITY

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Fig. 1.



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Fig. 2.



32X

Fig. 3.



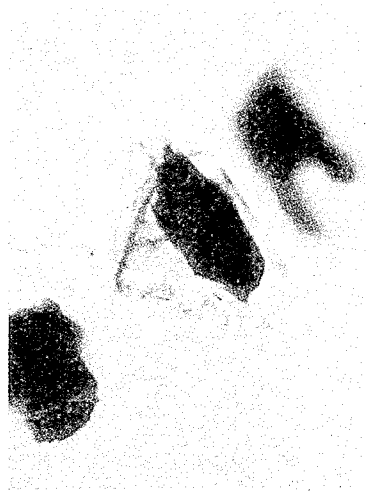
32X

Fig. 4.



100X

Fig. 5.



450X

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ANNEALED TITANIUM-BEARING SLAGS OF IMPROVED REACTIVITY

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10 Claims. (Cl. 252—182)

This invention relates to the production of titanium-bearing slags of improved reactivity in the sulfuric acid digestion processes used in titanium dioxide pigment manufacture and more particularly to slags of this type wherein the recoverable titanium dioxide-containing material is present in a coarsely crystalline condition separate from the sulfuric acid-insoluble materials in the slag.

Titaniferous slags are produced commercially by smelting iron-titanium ores, such as ilmenite, arizonite, nelsonite and the like, with carbonaceous reducing agents such as coal or coke and in the presence of basic fluxing agents such as lime, magnesia and alumina. The smelting is ordinarily carried out in electric furnaces at temperatures such that the entire mass, including the slag, is molten, such temperatures usually being above 2500° F. and ordinarily in the range of about 2700° F.–3200° F. Under these conditions most of the iron oxide is reduced to metallic iron and a part of the tetravalent titanium compounds of the ore are also partially reduced to a condition that is usually referred to as trivalent titanium. The metallic iron separates by gravity and forms a pool in the furnace while the unreduced iron oxide and the titanium compounds and other non-ferrous ingredients of the furnace charge collect as a supernatant slag layer.

During the furnacing process the magnesia, alumina and other basic constituents of the charge combine with titanium dioxide from the ore to form dititanates which crystallize out together when the slag is cooled. These basic constituents, including reduced or trivalent titanium and unreduced iron oxide in the slag are all isomorphous in the dititanate structure, and the compounds which they form with titanium dioxide are therefore designated simply as dititanates. They are frequently and properly expressed by the formula

$$(Mg, Fe, Ti)0.2TiO_2$$

The compound $Al_2O_3.TiO_2$ is isomorphous with the magnesium, iron and titanium dititanates of the above formula and is included within the general term dititanates. The compound $CaO.TiO_2$, known as perovskite, is not isomorphous in the dititanate structure, and when this compound is formed it appears in the cooled slags in a separate phase.

Slags of the type under consideration usually have a substantial content of silica, some of which originated in the ore and some in the coal or coke and/or fluxing agents used in smelting. In molten slags tapped from the smelting furnace this silica is contained in a glassy material that may vary from about 10% to 20% or more of the weight of the slag and is mixed homogeneously with the dititanate phase. Any perovskite that may be present is largely included in this phase. This glassy material is insoluble in sulfuric acid and therefore detracts from the commercial value of the slag; furthermore, as will subsequently be shown, it interferes with the extraction of the acid-soluble dititanates in the digestion process.

At present the titanium-bearing slags are tapped from

the smelting furnaces into a so-called slag casting machine wherein they are cast into slabs about 1 inch thick. The top and bottom surfaces of these slabs are cooled rapidly by water sprays to form a solidified outer skin, after which the slabs are dumped on a slag pile. Most of the slabs fracture when they fall on the pile and the fluid core of molten material spreads out in thin films and is quickly cooled. For reasons which will subsequently be explained, this haphazard method of cooling results in wide differences in the reactivity of different samples of the same slag toward sulfuric acid.

The present invention is based on the discovery that remarkable improvements in reactivity with sulfuric acid and in other desirable properties can be obtained by converting the originally homogeneous slag into a body of coarse dititanate crystals having the glassy material segregated at the interfaces thereof. Slags having such a phase separation, when ground, liberate the sulfuric acid-insoluble glassy material much more completely from the dititanate crystals, and the reactivity of the latter with sulfuric acid is therefore improved. Other important improvements in the digestibility of the slag, including a lower content of acid-insoluble rutile, are also obtained when the preferred methods of the present invention are used.

In accordance with the process of our invention the development of coarse dititanate crystals is obtained by an annealing process. The term annealing is employed in metallurgy to designate heat treating processes intended to modify the crystal structure of a metal or metal alloy; as used herein the term is most nearly analogous to the full annealing of ferrous alloys at temperatures above the transformation range to develop a desired crystal structure. By annealing titaniferous slags at temperatures above the freezing temperature of the glassy siliceous material and in the range where crystal growth of the dititanate phase occurs it is possible to effect a high degree of separation between the glassy material and the dititanate crystals so that the crystals will have a low content of sulfuric acid-insoluble material and the glass will have a low content of titanium dioxide values.

Slags of homogeneous structure produced by conventional cooling procedures can be annealed in accordance with our invention by reheating them to temperatures above the melting point of the glassy phase, which is about 2200° F., and holding them at these temperatures until crystals of the desired size have formed. Preferably, however, the process of our invention is applied to the molten slags as they are obtained from the smelting furnace by subjecting these slags to a controlled cooling in the range between the crystallizing temperature of the dititanates, which begins at about 2700° F., and the freezing temperature of the glassy material. This method of practicing our invention is analogous to the soaking of steel ingots since it applies a controlled cooling of an originally molten material to obtain a desired crystal structure and segregation of siliceous impurities.

We have found that dititanate crystals of substantial size can readily be obtained by applying the principles of our invention to any titaniferous slags containing dititanates in admixture with glassy siliceous material. At the present time these slags are produced by smelting ilmenite ores from the Murray Bay district of Canada, which ores contain alumina and magnesia and require very little added fluxing agents. It will be evident, however, that fluxing agents such as calcium oxide, magnesium oxide, alkali metal hydroxides or carbonates or the like may be added to any iron-titanium ores and the mixture smelted with coke to produce slags that can be treated in accordance with the process of our invention.

A wide variety of annealing processes may also be

employed. The slags may be cooled slowly through the critical range in insulated molds, or in furnaces similar to the soaking furnaces now employed by the steel industry, or the desired annealing temperatures may be maintained by direct impingement of flames if desired. An annealing procedure embodying the principles of our invention that is of particular commercial importance, however, consists in casting the molten slag into blocks of substantial size and allowing these blocks to cool slowly by radiation. Substantial improvements in reactivity have been obtained when the molten slag is cast into a cube having a side about 4 inches long, although this probably represents the minimum size for annealing by radiation without excessive insulation of the outer surfaces of the cube. In commercial practice slags having an excellent phase separation have been obtained by pouring the molten slag into roughly cubical or cylindrical masses weighing from 2 to 8 tons and allowing them to cool by natural convection cooling, and this constitutes a preferred practice of our invention. These masses, when cubical, will measure from 2.6 to 4.1 feet in each dimension.

The degree of growth of the dititanate crystals during the annealing of the slag constitutes an important control feature of our invention. In order to obtain a high degree of liberation of the dititanate phase from the glassy phase by grinding the crystals should be allowed to grow until their thickness is at least as great as the average particle size to which the slag is ground in preparing it for sulfuric acid digestion and preferably considerably greater. The particular size to which the slag is ground may vary considerably with the strength of the sulfuric acid to be used and with other variations in the digestion process, but is usually smaller than about 250—300 mesh. The dititanate crystals in the annealed slags should therefore have an average thickness greater than the size of a 300 mesh screen, and this average width or thickness is preferably greater than 150 microns. As will be shown by the following examples, dititanate crystals having an average width on the order of 250–400 microns are readily obtainable by the annealing process of our invention with a substantially complete segregation of the glassy siliceous material at the interfaces thereof.

The invention will be further described with reference to the accompanying drawings wherein:

Fig. 1 is a graph showing the improved reactivity of annealed slag as compared with quenched slag.

Fig. 2 is a photomicrograph at 32 diameters of a sample of quenched slag, showing the homogeneous distribution of the glassy siliceous material.

Fig. 3 is a similar photomicrograph of an annealed slag showing coarse crystals of the dititanate phase and the distribution of the glassy siliceous material at the interfaces thereof.

Fig. 4 is a photomicrograph at 100 diameters of a ground sample of the quenched slag of Fig. 2, showing how the small dititanate particles may be largely surrounded by the sulfuric acid-insoluble glassy phase, and

Fig. 5 is an enlarged picture of one of the slag particles of Fig. 4.

Fig. 1 is based on the test procedures described in Example 2 and shows clearly the increased reactivity of the annealed slags of the present invention as compared with portions of the same slag cooled by quenching. The commercial value of this increased reactivity is exhibited both by the higher recovery of titanium dioxide values shown on the drawing and in the additional important fact that digestions can be carried out with sulfuric acid of lower concentration at digestion temperatures if desired. In particular, the annealed slags of the invention are well suited for digestion with sulfuric acid of about 75% to 90% H_2SO_4 content.

A comparison of Figs. 2 and 3 of the drawings will show clearly the important differences in crystal structure and segregation of glassy material between the annealed slags and the quenched slag. These photomicrographs are described in detail in Example 3.

Fig. 4 of the drawings shows particles of the quenched slag of Fig. 2 after grinding to 325 mesh size. Their size range is about 44 to 60 microns. Even after this fine grinding it will be observed that many of the faces of the dititanate particles are covered by the sulfuric acid-insoluble glassy material, which prevents the attack of sulfuric acid at these faces. The adherence of the glassy material to a dititanate crystal is even more clearly shown in Fig. 5.

As has been stated, the best method of producing the annealed slags of our invention, from a practical standpoint, consists in simply pouring the molten slag from the electric furnace into blocks or molds of relatively large size and allowing these blocks to harden by convection cooling. The slag may be poured into molds lined with clay or sand, or may simply be run into a sand-lined trough or ditch and covered with sand or other insulating material to reduce the rate of cooling if desired. The particular cooling time will of course vary with the composition and temperature of the slag, but suitable times can easily be determined simply by observing the crystal structure. During the cooling process, as the slag cools through the range from about 2700° F. to about 2200° F. there is a rapid development of dititanate crystals, and the slag should be maintained within this temperature range for a time sufficient for these crystals to attain an average width of about 150 microns or greater. When this crystal size has been attained it will be found that most of the glassy siliceous material has segregated between the crystals so that a better separation is obtained when the slag is ground. Experience has shown that slags tapped from an electric furnace at temperatures in the range of 2700°–3000° F. and poured into blocks of substantial width and thickness weighing about 4–6 tons or more will develop the desired coarse crystal structure and siliceous phase separation with natural convection cooling; i. e., when these blocks are simply air-cooled without insulation. It will be understood that the outer surfaces of these blocks will solidfy promptly upon exposure to the mold, or to the air, but that the central portions will remain fluid and will cool much more slowly. Slag from the outer layers of the blocks will therefore have a considerably finer crystal structure than that from the central portions, which cool more slowly, and with much less segregation of glassy siliceous gangue; however, the average width of the dititanate crystals in the entire block will be greater than 150 microns and the reactivity of the entire mass of slag will be correspondingly improved.

Another important advantage obtained by hardening the slag in relatively large masses is the reduction of rutile formation therein. We have found that the reduced titania in the slag, which is believed to be present largely as $TiO.2TiO_2$, is oxidized readily upon exposure of the slag to air at high temperatures and that it is converted to rutile TiO_2 by this oxidation. Inasmuch as TiO_2 of rutile structure is insoluble in sulfuric acid, this oxidized material represents a loss in recoverable titanium values in the slag. By annealing the slag in relatively large masses a high volume to surface ratio is maintained, and the loss of titanium values through oxidation to rutile is correspondingly reduced. This oxidation can be still further reduced or entirely eliminated, if desired, by cooling the slag in the absence of air, as by employing completely closed molds, annealing furnaces from which air is excluded such as tunnel kilns and the like, or by cooling the slag from the furnace under a blanket of nitrogen, carbon dioxide or other inert gas. Other means of pouring and annealing the slag while preventing oxidation of the reduced titania will readily suggest themselves to those skilled in the art.

As an example of the foregoing the molten slag from the electric furnace may be tapped into molds which are passed through a tunnel kiln provided with an air lock

in each end. In such a kiln an inert atmosphere of nitrogen is quickly developed after the first few blocks of slag have consumed the oxygen in the air. If desired, however, a flow of gases from the electric furnace may be passed through this kiln; such gases usually contain about 55% of nitrogen, 28% of carbon monoxide, 13% of carbon dioxide and no oxygen, and are therefore well suited for the purpose. It will be understood that when a tunnel kiln heated by hot gases from the electric furnace or by other means is used it is not necessary to cast the slag into thick pieces; on the contrary, thin slabs ranging from 0.5–2 inches in thickness may be poured if desired since the requisite annealing is obtained by the heat of the furnace while the non-oxidizing atmosphere prevents the formation of rutile on the exposed surfaces of the slag.

From the foregoing it will be seen that our invention includes both novel procedures for the production of annealed slags of substantially increased reactivity and reduced rutile TiO_2 content and also a novel class of slag compositions characterized by coarse dititanate crystal structure and a high degree of segregation of glassy siliceous material at the interfaces of the dititanate crystals. These aspects of our invention will be further described and illustrated by the following examples.

Example 1

Slag was produced by smelting a charge of Allard Lake ilmenite from the Murray Bay district of Canada with coke in an electric arc furnace of commercial size by the procedure described in U. S. Patent No. 2,476,453 and at temperatures of about 3000° F. This slag was cooled by two different procedures. Sample No. 1 was run into shallow pans and cooled rapidly into slabs about one inch thick by quenching with water sprays. Sample No. 2 was run into insulated molds about three feet square and three feet deep and cooled by convection through the temperature range from 2700° F. to about 2200° F. and hardened into blocks weighing about three tons each. Both samples had the following gross chemical analysis:

Tetravalent titanium as TiO_2	50.0
Reduced titanium as Ti_2O_3	17.63
Iron as FeO	8.5
Aluminum as Al_2O_3	7.1
Magnesium as MgO	5.3
Calcium as CaO	2.2
Silicon as SiO_2	8.4

Specific gravity 3.75.

A portion of each of the samples weighing one kilogram was ground to an average particle size of about 44 microns and wet screened on a 325 mesh screen. The oversize material was dried, suspended in a heavy liquid of 3.2 specific gravity and separated into a sink fraction and a float fraction. The two float fractions were weighed and analyzed for titainum and the percent of slag and of glass was calculated from the titanium content. The results were as follows:

	Block Cast and Annealed	Pan Cast and Quenched
Percent of oversize floated	7.9	2.8
TiO_2 content, percent	22.7	38.9
Slag content, percent	33.2	55.5
Glass content, percent	66.8	44.5

These results show clearly that the glass phase is much more completely liberated from the dititanate phase in the annealed sample when the slags are ground to the particle size ordinarily used for sulfuric acid digestion.

Portions of the glass phase were separated from the two samples and analyzed. The results of these analyses are as follows:

	Sample No. 1	Sample No. 2
SiO_2	59.5	87.5
TiO_2	12.9	1.4
Al_2O_3	7.2	2.62
FeO	2.9	0.73
CaO	3.0	1.06
MgO	2.0	0.54

Specific gravity 2.8.

The increased silica content and the greatly decreased TiO_2 content in the glass from the annealed slag shows very clearly the high degree of phase separation obtained by the present invention. Very little of the dititanates were enveloped or occluded in the glass phase of the annealed slag to such an extent that they were not released upon grinding.

Example 2

Portions of the slag samples of Example 1 were ground to 325 mesh size and digested with sulfuric acid by a standard laboratory digestion procedure using acid having a content of 86% H_2SO_4 at reaction and varying weight ratios of acid (calculated as 100% H_2SO_4) to slag. The resulting digestion cakes were dissolved in water and the percent of TiO_2 recovered in soluble form was determined.

The results of these analyses are shown in Fig. 1 of the drawings which is a graph wherein the percent of TiO_2 recovery is plotted against the acid: ore ratio. These results show that the improved slags of the present invention will produce increased amounts of soluble titanium sulfates at any acid to slag ratio and also indicates that for any desired percent of recovery the ratio of acid to slag can be substantially reduced. For example the following acid:ore ratios to give a 90% recovery of solubilized titanium in a titanium sulfate liquor of 30% basicity are calculated from the curves of Fig. 1.

	Weight ratio of 100% acid to slag
Quenched slag	1.52
Annealed slag	1.46

The annealed slags can therefore be digested with about 4% less strong sulfuric acid than is necessary with quenched slags. Upon dissolving the resulting digestion cakes in water the basicity can be adjusted to the desired value, usually about 16%, *by* adding "end liquor" which is the dilute (20–25%) sulfuric acid obtained by hydrolyzing the titanium sulfate liquors. This is an important advantage, for it reduces materially the amount of waste sulfuric acid that must be disposed of as a water contaminant in a titanium dioxide pigment plant.

Example 3

Unground portions of the two slag samples of Example 1 were prepared in thin sections (0.002 inch thick) mounted on glass slides. These samples were examined under the microscope and the photomicrographs shown as Figs. 2 and 3 of the drawings were made at 32 diameters magnification. The photographs were taken by light passing through the samples; the opaque dititanate crystals therefore appear as dark masses on the prints while the light gray areas are the translucent siliceous gangue. The irregular white areas in Fig. 2 and the unshaded white areas in Fig. 3 are voids in the mounted samples.

The homogeneous character of the quenched slag of Fig. 2 is clearly shown. This slag consists of a uniform mixture of small dititanate particles having an average width of about 60 microns and thin layers or striations of siliceous gangue about 16 microns wide. These layers of sulfuric acid-insoluble siliceous material adhere to the dititanate phase after the slag is ground and reduce correspondingly the surface area that is open to attack by

the acid during digestion. This is shown in Fig. 4 of the drawings, which is a photomicrograph of the quenched slag of Example 1 ground to 325 mesh size. The photograph was taken by light transmitted through the sample and at 100 diameters magnification. The masking or shielding of entire sides or faces of a dititanate particle is further demonstrated in Fig. 5, which is an enlargement of a portion of Fig. 4.

Fig. 3 of the drawings shows that the annealed slag is a coarsely crystalline product composed of relatively large dititanate crystals with relatively thick masses of siliceous gangue segregated at the interfaces thereof. The dititanate crystals in this sample average about 250 microns in width and contain only minor inclusions of gangue. The glassy siliceous material averages about 95 microns in thickness and is therefore much more easily liberated from the titanate phase when the slag is ground, as has been demonstrated in Example 1.

The increased reactivity of the annealed slag, after grinding, is evident from its texture as shown in Fig. 3. Because the dititanate crystals are much larger in size than the corresponding particles of a quenched slag, it will be evident that the annealed slags are reactive with sulfuric acid even in a relatively coarse condition. Thus, such slags may be reacted with sulfuric acid after grinding to an average particle size within the range of about 250–300 mesh, whereas present practice with annealed slags requires that substantially all must pass through a 325 mesh screen.

Example 4

Samples of the two slags of Example 1 were ground and digested with 86% sulfuric acid as described in Example 2 and the resulting digestion cakes were leached with water to extract the resulting titanium sulfate. The undissolved residues from these extractions were filtered off and again digested with excess sulfuric acid, the mixture of acid and residue being heated to boiling in order to convert as much of the residue as possible into a soluble condition. The residues were again extracted with water, dried and weighed, and analyzed for titanium.

It was found that the titanium dioxide in the residue from the quenched slag amounted to 1.75% of the titanium in the original slag sample calculated as TiO_2; in other words, 1.75% of the total titanium values of the slag had been converted into rutile by oxidation during the cooling of the slag. The insoluble rutile titanium dioxide in the annealed slag was only 0.44% of the total TiO_2, expressed on the same basis. The effectiveness of pouring the slag into large masses as a means of reducing the extent of rutile conversion is clearly shown by this example.

What we claim is:

1. A method of improving the reactivity of titanium-bearing slags produced by smelting iron-titanium ores and containing dititanates together with smaller amounts of glassy siliceous material which comprises annealing said slags at a temperature between about 2700° F. and about 2200° F. and in the range between the crystallizing temperature of the dititanates and the freezing temperature of the glassy material in a mass weighing at least 4000 pounds and having a minimum dimension of at least 4 inches and thereby converting the originally homogeneous slag into a body of coarse dititanate crystals having an average thickness greater than the size of a 300 mesh screen having the glassy material substantially completely segregated at the interfaces thereof.

2. A method of improving the reactivity of titanium-bearing slags produced by smelting iron-titanium ores and containing dititanates together with smaller amounts of glassy siliceous material which comprises annealing said slags by maintaining them at a temperature between about 2700° F. and about 2200° F. and in the temperature range between the crystallizing temperatures of the dititanates and the freezing temperature of the glassy material in a mass weighing at least 4000 pounds and having a minimum dimension of at least 4 inches for a time sufficient to convert said dititanates into coarse crystals having a width greater than the average particle size diameter to which the slag is ground for digestion with strong sulfuric acid and having the glassy siliceous material substantially completely segregated at the interfaces thereof.

3. A method according to claim 2 wherein the slags are annealed to an average dititanate crystal width greater than 150 microns.

4. A method of producing titanium-bearing slags of improved reactivity which comprises smelting an iron-titanium ore with carbon at temperatures at which a homogeneous fluid slag containing dititanates and glassy siliceous material is formed, drawing off said slag and annealing it at a temperature between about 2700° F. and about 2200° F. and in the temperature range between the crystallizing temperature of the dititanates and the freezing temperature of the glassy siliceous material in a mass weighing at least 4000 pounds and having a minimum dimension of at least 4 inches for a time sufficient to convert said dititanates into coarse crystals having an average width of at least 150 microns with the glassy material substantially completely segregated at the interfaces thereof.

5. A method of improving the reactivity of titanium-bearing slags produced by smelting iron-titanium ores at temperatures at which a homogeneous fluid slag containing dititanates and glassy siliceous material is formed which comprises annealing said slags by casting them into masses having a minimum dimension of at least 4 inches and weighing at least 4,000 pounds and cooling said masses by convection through the temperature range of 2700° F. to 2200° F. whereby the slag is converted into a body of coarse dititanate crystals having the glassy siliceous material substantially completely segregated at the interfaces thereof.

6. A method according to claim 5 wherein the slag is cast into masses weighing about 4 to 8 tons each.

7. A method of improving the reactivity of titanium-bearing slags produced by smelting iron-titanium ores and containing dititanates including compounds of reduced titanium together with smaller amounts of glassy siliceous material which comprises annealing said slags at a temperature between about 2700° F. and about 2200° F. and in the range between the crystallizing temperature of the dititanates and the freezing temperature of the glassy material in a mass weighing at least 4000 pounds and having a minimum dimension of at least 4 inches for a time sufficient to convert said dititanates into coarse crystals having an average width greater than 150 microns with the glassy siliceous material substantially completely segregated at the interfaces thereof while preventing oxidation of said compounds of reduced titanium by excluding oxygen from said slag.

8. A method according to claim 7 wherein the slag is annealed in a blanketing atmosphere of non-oxidizing gas.

9. A method according to claim 7 wherein the slag is annealed by soaking in closed molds.

10. A titanium-bearing slag of improved reactivity consisting essentially of a mass of coarse dititanate crystals substantially free from sulfuric acid-insoluble material and having an average width greater than 150 microns with glassy siliceous gangue substantially completely segregated at the interfaces thereof.

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