SMELTING PROCESS FOR RECOVERING COLUMBIUM AND/OR TANTALUM FROM LOW GRADE ORE MATERIALS CONTAINING SAME

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Columbium - Tantalum Metallurgical Concentrate

Carbon (e.g. coke)  Iron (if required)  Lime (as flux)

Smelting Furnace (1200°-1600°)

Molten Columbium-Iron-Carbon Matrix Metal

Slag

Granulation

Granulated Matrix Metal

Acid Leach (for removal of iron)

Ferrous Salts

Crude Columbium-Tantalum Carbide

To discard

Caustic Soda Leach (for removal of Silicon)

Silicon Salts

Columbium-Tantalum Carbide Powder

To Market or Further Processing

INVENTOR.

STUART R. ZIMMERLEY
ALEXANDER EDWARD BACK

ATTORNEYS
This invention relates to processes for treating columbium and tantalum bearing materials, such as ores and ore concentrates, and is concerned particularly with effectively increasing the relative content of low grade ore materials, while at the same time effectively decreasing the gangue content thereof.

The process involves the provision of a multi-phase molten system in which columbium and tantalum carbides are collected in a molten metal phase and gangue materials are collected in a slag phase, such gangue materials being rejected by pouring off the molten slag.

This is particularly important in the treatment of low grade ores and concentrates where the gangue constituents form the major portion of the material being treated. By the process, it is possible to accomplish the desired collection in a smelting procedure carried out at a temperature low enough to permit the use of a standard electric smelting furnace.

Columbium, or niobium as it is usually referred to from a chemical standpoint, is a metallic element occurring naturally in various mineral forms in association with the metallic element tantalum. The latter element is present to a much lesser extent than the former. Accordingly, though the description herein may apply columbium alone, it should be borne in mind that it applies with equal force to tantalum if that element predominates in the minerals concerned or is the value particularly sought.

The mineral columbite makes up the richest of the known columbium ores, and has been the only significant source of columbium up to the present time. However, it now appears that there are large available reserves of columbium in the form of carbonatite type ores containing such columbium minerals as perovskite, pyrochlore, and nioculite.

Because these minerals contain themselves less of the element columbium than does columbite, commercial exploitation thereof has not heretofore been economically feasible. Columbium mineral concentrates obtainable from such low grade ores by various beneficention procedures are ordinarily considerably lower in columbium content than columbite concentrates and contain large quantities of closely associated gangue minerals, which act as especially undesirable diluents to the desired columbium values.

It has not been possible to utilize these low grade concentrates in the same manner as high grade columbite concentrates. The latter normally contain more than 50% combined columbium and tantalum oxides, as against from approximately 1% to 15% normally present in the former.

The high grade columbite concentrates are ordinarily reduced to ferrocolumbium by a thermite type of reaction, the ferrocolumbium so produced being used primarily for alloying purposes in the steel industry. It has been proposed to produce columbium metal from ferrocolumbium by a chlorination and reduction procedure.

However, the chlorination temperatures involved in order to keep ferrous chloride from plugging up the system are relatively high, i.e., in the order of 1,000° centigrade. While the low grade concentrates cannot be successfully reduced to ferrocolumbium by the above process, we have found that they may be treated by direct chlorination at temperatures between approximately 600° to 900° centigrade. However, chlorine-consuming constituents other than columbium and tantalum, e.g., iron, calcium, magnesium, react with the chlorine to produce respective chlorides which are plastic at the chlorination temperatures and prevent efficient operation of the chlorinating procedure.

Columbium metal cannot be produced from the high grade columbite concentrates by conventional smelting methods, because of the formation of insusible carbides, see page 317 of the authoritative text "Electric Melting and Smelting Practice", by A. G. E. Robertson, published by Charles Griffin & Co. Ltd., London, in 1955, nor can columbium metal be successfully produced by smelting the low grade concentrates obtained from carbonatite type ores.

The present invention is concerned with the upgrading of such low grade concentrates by carbiding the columbium content thereof, which we have found places them in condition for effective utilization, primarily halogenation for the production of a columbium halide. From such halide, there may be produced by known procedures columbium oxide and other compounds of columbium, as well as columbium metal.

In accordance with the invention, the low grade concentrate is subjected to a high-carbon smelting procedure in the presence of iron. The carbon combines with the columbium to form columbium carbide, which is collected by the molten iron functioning, in effect, as a matrix. Given enough iron in the furnace charge, separate fluid metallic and slag phases will result, which may be tapped separately. The metallic phase contains essentially all of the columbium as the carbide, while the slag phase contains the gangue.

It has heretofore been proposed to subject ore and other metallurgical materials containing columbium-tantalum to a reducing operation in an electric furnace in the presence of carbon to produce a slag rich in columbium-tantalum and a ferro-alloy in which the impurities are concentrated by virtue of the collecting action of the carbon. The slag is treated to produce a commercial ferro-columbium-ferrotantalum. The ferro-alloy contains some columbium-tantalum, and constitutes an impure ferrocolumbium-ferrotantalum which may be subjected to further carburization by smelting in the presence of carbon.

In contrast with such procedure, wherein the columbium-tantalum is significantly divided between a slag phase and a ferro-alloy phase, the process of the invention involves smelting of the primary ore or ore concentrates with sufficient carbon in the first instance to carbide essentially the entire columbium-tantalum content. We have found that, when this is done, the iron present acts as a matrix to collect such columbium-tantalum content selectively as against the gangue, which gangue forms a fluid slag that can be easily drawn off separately from the metallic phase.

The customary low grade concentrates are normally high enough in iron content to bring about the desired fluid metallic and slag phases in the smelting operation without the addition of iron.

Advantages of the present process include the obtaining, in a single carbidizing-smelting step, of an exceptionally high degree of separation of the columbium from associated gangue constituents; the production of a greatly en-
riced columbium-bearing material in a form peculiarly adapted for effective halogenation; and the making possible elimination, by means of a simple leaching step, of a major portion of the iron content on a selective basis as respects the columbium present.

One aspect of the invention involves production of considerably purer halogen salts of columbium than heretofore and ultimately columbium metal from heretofore unusable, low grade ores at significantly lower temperatures and with significantly less consumption of halogen and with a substantial reduction in the usual corrosion problems.

Further advantages and features of the invention will become apparent from the following description of presently preferred practice of the process as outlined in the accompanying drawing.

The single figure of the drawing is a flow sheet representing a typical application of the process in practice.

In accordance with the process and as indicated by the flow sheet, smelting is accomplished in suitable apparatus, such as an electric furnace. To the columbium ore or concentrate is added carbon in some practical form, for example coke, calcium carbide, or some other suitable carbon-containing material, together with additional iron and flux if required or found desirable in any particular instance.

The carbon is utilized in sufficient quantity to more than account for the columbium, as columbium carbide, in the metallic phase. In other words, an excess of the stoichiometric equivalent of the carbon necessary to reduce the columbium content to columbium carbide is required. The extent of such excess will depend upon the extraneous carbon-consuming constituents present in any given instance. The quantity for any given furnace charge may be easily determined on the basis of the columbium content of such charge, due allowance being made for carbon-consuming side reactions.

In a presently preferred practice applied to a low grade columbium metallurgical concentrate obtained from carbonatite type ore and having a columbium content within the range of approximately 1% to 15% and an iron content within the range of approximately 6% to 13%, the finely divided concentrate is added carbon in some practical form, for example coke, calcium carbide, or some other suitable carbon-containing material, together with additional iron and flux if required or found desirable in any particular instance.

The carbon is utilized in sufficient quantity to more than account for the columbium, as columbium carbide, in the metallic phase. In other words, an excess of the stoichiometric equivalent of the carbon necessary to reduce the columbium content to columbium carbide is required. The extent of such excess will depend upon the extraneous carbon-consuming constituents present in any given instance. The quantity for any given furnace charge may be easily determined on the basis of the columbium content of such charge, due allowance being made for carbon-consuming side reactions.

In a presently preferred practice applied to a low grade columbium metallurgical concentrate obtained from carbonatite type ore and having a columbium content within the range of approximately 1% to 15% and an iron content within the range of approximately 6% to 13%, the finely divided concentrate (ordinarily available at approximately minus 100 mesh) is charged into the smelting furnace along with an appropriate weight of metallurgical coke, usually within the range of from 8% to 12% of the weight of the concentrate, and is smelted at a temperature of approximately 1200° to 1600° centigrade. Two distinct and separable products are obtained, namely, a free-flowing, liquid, substantially columbium-free slag and a free-flowing, molten, iron matrix phase containing essentially all of the columbium content of the concentrate as columbium carbide.

The slag is made up of the gangue constituents. Data obtained from numerous laboratory tests have consistently shown not more than from 0.03% to 0.1% \( \text{C}_2\text{O}_3 \) in such slag, which indicates a recovery of from 90% to 98% of the columbium in the concentrate.

The metallic phase of matrix metal is a columbium-iron-carbon system containing certain impurities, notably silicon. The assay of a typical matrix metal produced in this manner from a low grade concentrate containing 2.5% \( \text{C}_2\text{O}_3 \) and derived from carbonatite type ore of the Oka deposit in Quebec Province, Canada, showed 17.0% \( \text{C}_2\text{O}_3 \) as columbium carbide, 57.5% iron, and 10% silicon. Coke was included in the charge at the smelting furnace to the extent of 10% of the weight of the ore concentrate.

Other tests have yielded matrix metal assaying as high as 22% \( \text{C}_2\text{O}_3 \), approximately 58% iron, and as low as 2% silicon.

There appears to be a limit to the quantity of columbium carbide that can be concentrated in a given quantity of iron. Tests indicate that too great a columbium to iron ratio will change the free-flowing, molten iron matrix to a mush which cannot be readily removed from the furnace.

In a present practice, at least four parts of iron are necessary for every part of columbium oxide present in the furnace charge if the resulting metallic phase is to be free flowing and capable of being satisfactorily tapped.

It is desirable that the matrix metal tapped from the smelting furnace be run directly into water, usually a high pressure stream, to produce an easily handled, more malleable product. Even though such product is high in iron and silicon, it may be halogenated for the production of columbium metal or utilized for other purposes. We prefer, however, to regard it as an intermediate product and to further upgrade by the removal of iron and silicon to prepare a more suitable feed for halogenation.

Iron is removed from such intermediate product by acid leaching. As a preferred leaching procedure, twice the stoichiometric amount of a 15% to 20% sulfuric acid solution is applied to the granulated iron matrix and allowed to remain until the available iron is dissolved, usually from 18 to 24 hours.

The crude columbium carbide resulting from this leaching stage is then subjected to further leaching with a strong alkali, for example and preferably sodium hydroxide, for the removal of silicon. We prefer to add twice the stoichiometric amount of a 20% sodium hydroxide solution to the crude columbium carbide and permit the leaching to continue until the available silicon is dissolved, usually from 4 to 6 hours. The resulting columbium carbide is a fine powder which has proven particularly amenable to halogenation.

Halogenation of the columbium carbide, whether in granular, powdered, or briquet form, is effected by feeding it into a stream of halogen gas, usually chlorine, or by introducing the gas into a charge of the carbide to form chlorides. A significant feature of the fact that columbium pentachloride (\( \text{CbCl}_5 \)) is the reaction product, rather than the less desirable mixture of \( \text{Cb} \) and columbium oxychloride which results from chlorination of other types of columbium-bearing materials.

The columbium pentachloride may be reduced by magnesium metal in known manner to form a columbium metal sponge of exceptionally high purity.

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Production of columbium carbide in a resistance furnace from high grade columbium concentrate would require temperatures above those which the usual furnace lining is capable of withstanding. It also would involve a considerable length of time. The significance of lower temperatures involved in the present process and the much shorter time required, as well as the ease of handling the resulting carbide product, more than make up for the leaching step to remove the added iron.

Whereas this invention is herein set forth in specific detail with respect to preferred practice thereof, it should be realized that various changes may be made without departing from the generic teachings hereof.

We claim: A metallurgical upgrading process, comprising smelt-
ing a low grade concentrate of a carbonatite type ore, which contains from approximately 1 to 15 percent combined columbium and tantalum oxides as one or more of the minerals perovskite, pyrochlore, and niocalite intimately intermixed with associated gangue materials, at a temperature of about 1200° C. to 1600° C. in the presence of sufficient carbon to form columbium and tantalum carbides and at least four parts of iron, by weight, to each part of columbium oxide, to form a molten metallic matrix which collects the columbium and tantalum carbides and leaves gangue constituents as a molten slag; and drawing off said molten slag and said molten matrix separately.

References Cited in the file of this patent

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