United States Patent Office

3,057,714

Patented Oct. 9, 1962



3,057,714

# PYROMETALLURGICAL PROCESS FOR THE SEPARATION OF COLUMBIUM AND TANTALUM

Alexander E. Back, Russell R. Beck, and Clifford E. Selin, Salt Lake City, Utah, assignors to Kennecott Copper Corporation, New York, N.Y., a corporation of New York

No Drawing. Filed Aug. 20, 1959, Ser. No. 834,912
10 Claims. (Cl. 75—1)

This invention relates to processes for the separation of tantalum values from columbium values contained by ores, ore concentrates, and other mineral materials.

Columbium and tantalum values generally coexist in the natural mineral form, the proportion of one to the other varying over a wide range in different ore deposits. While in some instances the tantalum content is negligible, in most instances there are economically significant quantities of both present in the ore. This is particularly true with high grade columbite ores.

Due to the chemical similarity of columbium and tantalum, their separation has been extremely difficult and expensive. For example, it has been found necessary in the past to fuse a columbium-tantalum concentrate with alkali compounds at a temperature in the range of from 700° to 900° C. and to subject the fused product to leaching, filtration, digestion, and chemical reaction steps in order to produce columbium and tantalum compounds which could be separated by a fractional crystallization technique.

Mineral concentrates and other metallurgical products containing columbium and tantalum in various proportions are widely used in industry. Yet, there are specific demands for materials which contain an unusually high ratio of columbium to tantalum and vice versa.

A principal object of the present invention is to provide a relatively economic process for treating mineral materials which contain significant quantities of both columbium and tantalum values, to recover essentially all of the columbium in a product in which the ratio of columbium to tantalum is considerably higher than in the starting material, and to recover a major part of the tantalum in a product in which the ratio of tantalum to columbium is considerably higher than in the starting material.

Briefly, the process of this invention comprises smelting a columbium-tantalum mineral material, intermixed with sulfur or a sulfur-bearing material, carbon, and either a basic or an acidic fluxing agent, such as lime or silica, respectively, in controlled quantity, to produce a matte product relatively rich in columbium as respects tantalum and a slag product relatively rich in tantalum as respects columbium. As in matte smelting in general, iron should be present to a limited extent.

Matte smelting has been applied heretofore on an experimental basis to columbium-bearing black sands, or ilmenite, obtained as an intermediate product in the processing of Arkansas bauxite. It was found that the relatively small columbium content (about 0.6% Cb) was largely concentrated in the matte, along with the major constituent, titanium, see pages 19–21 of U.S. Bureau of Mines Report of Investigations 5064, July 1954, entitled "Progress Report on Development of Columbium in Arkansas for 1953" by V. A. Nieberlein et al. It is extremely doubtful whether any tantalum was involved in these experiments. If so, it is apparent that the quantity was so small as to be negligible and beyond practical analysis.

In work done prior to the present invention involving the smelting of columbium-tantalum ore materials, see the copending application of Stuart R. Zimmerley et al., Serial No. 679,889, filed August 23, 1957, now Patent No. 2,972,530, granted February 21, 1961, entitled "Smelting Process for Treating Columbium and Tantalum Bearing Materials," it was found that the tantalum remained with the columbium in a matrix metal product in which the columbium was concentrated. Accordingly, we were much surprised to note the selective concentration of tantalum in the slag, as against columbium in the matte, in experiments leading up to this invention.



A feature of the invention, then, is the application of matte smelting practice to mineral materials containing significant quantities of both columbium and tantalum values, to achieve a separation of such values.

In carrying out the process, the columbium-iron-sulfur ratio of the charge should be adjusted in accordance with good matte smelting practice. There must be sufficient sulfur present in the charge to satisfy the columbium and iron content thereof stoichiometrically. An excess of iron is not detrimental so far as Cb-Ta separation is concerned. If sufficient iron is not present in the columbium-tantalum mineral material to be treated, it may be added by utilizing iron pyrite as the sulfidizing agent, or, if sulfur or some iron-free sulfur compound is employed as the sulfidizing agent, it may be added to the charge in any other suitable manner. Regardless of the iron content of the mineral material to be treated, iron pyrite is the preferred way of adding sulfur to the charge.

Our work has indicated that there is no critical smelting temperature range applying to all possible mineral materials. The several specific materials tested were smelted within a temperature range of 1300° to 1550° C. Yet, somewhat lower and considerably higher temperatures are indicated for other mineral materials having different components and analyses, and may be chosen as deemed proper by those skilled in the metallurgical art.

A significant advantage of the process is that a high columbium, low tantalum metallurgical product may be produced in a single smelting step from a material containing significant amounts of both columbium and tantalum.

Highly siliceous slags have been found more suitable for the separation of columbium and tantalum values than neutral or basic slags when columbite is the mineral involved. Best results have been obtained by adjusting the composition of the charge by addition of lime or silica to produce slags with an $SiO_2$ to CaO ratio ranging from 2.0:1 to 2.7:1. In adjusting the charge, the addition of either the basic or the acidic fluxing agent is controlled in amount by the lime and silica content of the raw materials.

On the other hand, when low grade, pyrochlore-perovskite concentrate is the mineral material, a neutral or basic slag gives the best results. The composition of the charge should be adjusted to produce a slag having a CaO to $SiO_2$ ratio of 1:1 to 1.3:1.

Carbon is required as a reducing agent in all instances. Satisfactory results have been obtained by adding coke in controlled amounts effective to leave a slight excess on top of the slag at the end of the heat.

The following examples are typical of presently preferred procedures in the carrying out of the process, and the results obtained are representative of what may be expected from the process:

*Example 1*

A 215 gram sample of columbite concentrate containing 46.7 percent columbium and 6.2 percent tantalum, 0.01% lime, and 1.7% silica was mixed with 20 grams of lime in order to properly adjust the silica-lime content, 50 grams of coke, and 215 grams of pyrite concentrate containing 41.4 percent iron and 47.3 percent sulfur. The mixture was smelted in a graphite crucible at a tem-

perature of 1420° C. to obtain a molten, two phase system consisting of immiscible slag and matte products. After the charge had fused, the melt was held at 1420° C. for 45 minutes. It was then allowed to solidify in the crucible. On analysis, it was found that the matte product contained 34.6 percent columbium and 0.9 percent tantalum, with an iron content of 36.5 percent and a sulfur content of 17.3 percent. The slag product contained 6.7 percent columbium and 15.8 percent tantalum, with an iron content of 1.8 percent.

Thus, starting with columbite containing Cb and Ta in the ratio of 7.5:1, a matte product was obtained with a Cb/Ta ratio of 39.6:1, and a slag product with a Cb/Ta ratio of 0.42:1.

*Example 2*

A similar 215 gram sample of columbite concentrate was mixed with 215 grams of a similar pyrite concentrate, 20 grams of lime, and 65 grams of coke. Half of the mixture was melted in a graphite crucible, after which the balance of the charge was added to the melt. The melt was held at a temperature of 1500° C. for a period of 40 minutes and then allowed to solidify in the crucible. The products obtained by this treatment were a matte containing 30.2 percent columbium and 0.6 percent tantalum, with an iron content of 40.8 percent and a sulfur content of 19.7 percent, and a slag containing 1.4 percent columbium and 10.8 percent tantalum, with an iron content of 2.0 percent.

Here, then, starting as in Example 1 with columbite concentrate containing Cb and Ta in the ratio of 7.5:1, a matte product was obtained with a Cb/Ta ratio of 50.4:1, and a slag product with a Cb/Ta ratio of 0.13:1.

*Example 3*

A generally similar procedure was employed for several tests utilizing respective samples of relatively low grade columbium-tantalum concentrate containing 7.4 percent columbium, 0.3 percent tantalum (24.7:1 ratio) as pyrochlore and perovskite minerals, 18.2% lime, and 19.1% silica. The same pyrite concentrate was utilized as in the foregoing examples. In one test, with temperature at 1450° C., a matte product was obtained with a Cb/Ta ratio of 132.5:1, and a slag product with a Cb/Ta ratio of 7:1. In two other tests, with temperatures of 1450° C. and 1400° C., respectively, matte products were obtained with Cb/Ta ratios of 70.0:1 and 186.0:1, respectively, and slag products with Cb/Ta ratios of 6.0:1 and 12.0:1, respectively. Since silica and lime were in proper balance in the mineral material used for these tests, no flux addition was required. However, other tests have shown that when silica and lime are not in balance, controlled flux addition may be utilized to obtain satisfactory results.

It will be noted from the tests of Example 3 that, because of the small quantity of tantalum present in the feed concentrate, there was little or no upgrading of tantalum in the slag. In commercial operations, this slag would be ordinarily discarded, since the tantalum content is not sufficient for economic recovery. The advantage of the present process with these low grade ores is the separation from the columbium of what little tantalum is present in the mineral material.

Repeated laboratory tests have shown that, in general, for the high grade, columbite concentrates, ratios of concentrate to pyrite (38% to 41% Fe) of from about 1:0.3 to about 1:2 by weight should be used. The iron content of the matte should be in the range of about 34 to 38% Fe and the sulfur content in the range of about 14 to 19% S. The iron content of the slag should be from 2 to 5% Fe. The smelting temperature may range from 1400° to 1500° C. For the lower grade pyrochlore and perovskite concentrates, ratios of concentrate to pyrite of from about 3.0:1.0 to about 6.5:1.0 by weight, depending upon the columbium-tantalum content of the concentrate, should be used. The iron content of the matte should be in the range of from 40 to 55% Fe and the sulfur content in the range of from 8 to 23% S. The iron content of the slag should be in the range of from 2 to 5% Fe. The smelting temperature may range from 1300° to 1550° C.

The columbium mattes can be used as starting material for the production of higher grade chloride or oxide products containing higher Cb:Ta ratios than the starting material.

The high tantalum slags are useful for reduction to matrix metal as disclosed in the aforementioned Zimmerley et al. application Serial No. 679,889. Moreover, they can be reduced to ferrotantalum by standard procedures, and the ferrotantalum is amenable to chlorination to produce tantalum pentachloride and, ultimately, tantalum metal in known manner.

Whereas this invention is here described with respect to certain presently preferred procedures, it should be understood that various changes may be made without departing from the essential inventive concepts disclosed herein.

We claim:

1. A pyrometallurgical process for the separation of tantalum values from columbium values in a mineral material containing significant quantities of both along with a significant quantity of slag-forming material, comprising smelting such mineral material together with sulfur and carbon, and with iron in sufficient amount in said material to form a matte, there being sufficient sulfur to satisfy the columbium and iron stoichiometrically so as to produce a matte product in which the ratio of columbium to tantalum is considerably higher than in the starting material and a slag in which the ratio of tantalum to columbium is considerably higher than in the starting material, the said matte containing essentially all of the iron; and drawing off said matte product separately from said slag product.

2. The process of claim 1, wherein the mineral material is columbite, and the smelting charge is adjusted with respect to silica and lime to produce an acidic slag.

3. The process of claim 1, wherein the mineral material is a low grade pyrochlore-perovskite concentrate, and the smelting charge is adjusted with respect to silica and lime to produce a basic slag.

4. The process of claim 1, wherein the sulfur component of the charge is provided by iron pyrite.

5. The process of claim 2, wherein the smelting charge is adjusted with respect to silica and lime to produce an acidic slag having an $SiO_2$ to CaO ratio substantially within the range of 2.0:1 to 2.7:1.

6. The process of claim 3, wherein the smelting charge is adjusted with respect to silica and lime to produce a basic slag having a CaO to $SiO_2$ ratio substantially within the range of 1:1 to 1.3:1.

7. A pyrometallurgical process for the separation of tantalum values from columbium values in a columbite mineral material containing a significant quantity of slag-forming material, comprising smelting said mineral material together with carbon, iron, and sulfur at a temperature substantially within the range of from 1400° to 1500° C. to form a matte and a slag, the sulfur being in amount sufficient to satisfy the columbium and iron stoichiometrically, said matte containing the major proportion of the columbium and essentially all of the iron, said slag containing the major proportion of the tantalum and being immiscible in the matte; and separating the matte and the slag.

8. The process of claim 7, wherein the mineral material is an ore concentrate.

9. A pyrometallurgical process for the separation of tantalum values from columbium values in a low grade, pyrochlore-perovskite, mineral material containing a significant quantity of slag-forming material, comprising

smelting said mineral material together with carbon, iron, and sulfur at a temperature substantially within the range of from 1300° to 1550° C. to form a matte and a slag, the sulfur being in amount sufficient to satisfy the columbium and iron stoichiometrically, said matte containing the major proportion of the columbium and essentially all of the iron, said slag containing the major proportion of the tantalum and being immiscible in the matte; and separating the matte and the slag.

10. The process of claim 9, wherein the mineral material is an ore concentrate.



**References Cited** in the file of this patent

UNITED STATES PATENTS

2,004,498 Becket ---------- June 11, 1935

OTHER REFERENCES

Nieberlein et al.: "Progress Report on Development of Columbium in Arkansas for 1953." Bur. of Mines Report of Investigations 5064. Entire report 27 pages. Pages 18–21 pertinent. Published July, 1954, by Bur. of Mines, D.C.

Hampel: Rare Metals Handbook, page 389, published 1954 by Reinhold Publ. Corp., N.Y.