United States Patent Office

2,905,548

Patented Sept. 22, 1959

2,905,548

METHOD OF RECOVERING TANTALUM AND COLUMBIUM

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No Drawing. Application September 6, 1957
Serial No. 682,287

20 Claims. (Cl. 75—84)

This invention relates to a method of recovering tantalum and columbium from their ores.

This is a continuation-in-part of United States patent applications Serial Numbers 534,610, filed September 15, 1955, now abandoned, and 239,393, filed July 30, 1951, now abandoned.

In the case of tantalum or columbium, these metals cannot be recovered from tantalite, columbite and similar ores by a smelting process, nor can they be obtained by a reduction of the oxides with hydrogen. Under the present process, these ores are fused with caustic soda to convert the tantalum and columbium into a fused mass of crude sodium tantalate and sodium columbate mixed with a number of impurities. After cooling, the fused mass is crushed and the water soluble impurities removed by leaching with water. The acid soluble impurities are then removed by treating the mass with hot hydrochloric acid. This converts the sodium tantalate and sodium columbate into insoluble tantalic and columbic acids. This mixture of acids is then dissolved in hot hydrofluoric acid and potassium carbonate is added to form the double salts, potassium tantalum fluoride and potassium columbium oxyfluoride. The hot solution is then cooled. The potassium tantalum fluoride crystalizes out leaving the potassium columbium oxyfluoride in solution. The columbium salt is then recovered from the solution.

The pure tantalum and columbium metals may be obtained directly from the double fluorides by electrolysis of the respective fused salts. Also, the salts may be converted to oxides by treating the same with an alkaline solution such as sodium hydroxide after which the resulting salt is washed and then treated with an acid such as hydrochloric acid after which the resulting powder is washed. When tantalum is treated this way the resulting oxide is an hydrated oxide (Ta_2O_5—H_2O).

When the pure tantalum and columbium metals are obtained by electrolysis, the metal become dispersed as fine grains or powder in the salt mass as electrolysis progresses. After electrolysis, the salt mass is crushed and the metal recovered from the crushed mass.

The electrolysis of the fused tantalum or columbium metal salts is a costly operation. Recovery of the tantalum or columbium metal from the oxides thereof is also a costly operation. The new method of this invention provides a more economical means for the production of tantalum and columbium and eliminates many of the costly steps heretofore used in recovering the metals from the salts or oxides.

In our co-pending United States patent application, Serial Number 534,609, filed September 15, 1955, now abandoned, which is a continuation-in-part of our United States patent applications, Serial Number 195,910, filed November 15, 1950, now abandoned, and Serial Number 239,391, filed July 30, 1951, now abandoned, we have disclosed and claimed a method for the recovery of refractory metals including tantalum and columbium whereby the double salt of tantalum or columbium (as for example potassium tantalum fluoride and potassium columbium oxyfluoride) is first reacted with aluminum forming an intermetallic compound or alloy of aluminum and tantalum or columbium. The intermetallic compound or alloy is reacted with a third metal, such as copper, silver or gold which is substantially insoluble in the tantalum or columbium, but which alloys with the aluminum. As a result, the tantalum or columbium is obtained in substantially pure form as finely divided particles dispersed throughout the aluminum-third metal alloy.

We have discovered that tantalum or columbium can be recovered from its compound by heating the tantalum or columbium compound with an alloy of aluminum and a third metal, such as copper, silver or gold, which is substantially insoluble in tantalum or columbium. The resulting mixture includes columbium or tantalum dispersed therethrough in a finely divided, substantially pure state. The substantially pure tantalum or columbium is then separated from the mixture.

To simplify the description of the new method, reference is made specifically to the preparation of tantalum and columbium from potassium tantalum fluoride, tantalum oxide, potassium columbium oxyfluoride and columbium pentoxide. It is understood that the method is applicable to other compounds of tantalum and columbium.

In reacting, for example, an aluminum-copper alloy with potassium tantalum fluoride, the potassium tantalum fluoride may be placed in a crucible or other container, and the potassium tantalum fluoride covered with a graphite plate. The alloy may be placed on the graphite plate and the mass covered with a suitable slag material such as sodium chloride. The graphite plate retains the aluminum-copper alloy above the potassium tantalum fluoride until the alloy becomes molten. This prevents the alloy from settling at the bottom of the crucible before contacting and reacting with the potassium tantalum fluoride. The mass is then heated; the molten aluminum-copper alloy is allowed to contact the potassium tantalum fluoride; and reaction occurs. The resulting mass may be agitated with a graphite rod or other inert material to insure a thorough mixing of the salt and the aluminum-copper alloy.

The mass resulting from the above reaction includes tantalum in a finely divided, substantially pure state dispersed therethrough as well as aluminum fluoride and potassium fluoride. The fluorides may be volatilized or may remain as a constituent of the slag, depending upon the temperature of the mass. The tantalum is recovered from the ingot by dissolving the copper or an alloy of aluminum and copper remaining in the mass in nitric acid, following which the tantalum is washed free of acid and dried.

In the event that the equivalent of three mols of potassium tantalum fluoride is reacted with five mols of copper-aluminum alloy, then the reduction of the potassium tantalum fluoride or the reaction of this salt with the aluminum-copper alloy may be represented by the following theoretical equation:

$$3K_2TaF_7+5CuAl\rightarrow 5AlF_3+6KF+5Cu+3Ta$$

It is readily seen that under such conditions the mixture resulting from the reaction between the aluminum-copper alloy and the potassium tantalum fluoride includes aluminum fluoride, potassium fluoride, free copper and substantially pure tantalum dispersed as minute grains throughout the body of the mixture. Since the copper and tantalum are mutually insoluble, the tantalum is readily separable from the mixture, as by dissolving the copper in nitric acid and then washing the tantalum free of acid.

In the event that a smaller proportion of aluminum is used in the reaction, then only some of the tantalum will be recovered and a portion of potassium tantalum fluoride will remain.

To ensure optimum recovery of tantalum, it is preferred to employ an excess of the aluminum-third metal alloy. Under such conditions the product resulting from the reaction of the aluminum-third metal (copper, gold or silver) alloy with, for example, potassium tantalum fluoride, includes aluminum fluoride, potassium fluoride, aluminum-copper alloy and tantalum metal in a finely divided, substantially pure state dispersed throughout the metallic portion. Under such conditions, substantially all of the fluorides remain as constituents of the slag. Since the tantalum is substantially insoluble in the copper-aluminum alloy, it may be recovered from the reaction mixture by dissolving the alloy in nitric acid, following which the tantalum is washed free of acid and dried.

In recovering the tantalum metal from tantalum oxide, the method is substantially identical to the method employed when recovering the metal from the halide except that a fluxing agent such as an alkali metal halide flux is added to the oxide powder.

The new method of this invention for the recovery of tantalum and columbium from their respective compounds may be illustrated by the following specific examples:

Example 1

An aluminum-copper alloy was prepared by melting 15 parts by weight of aluminum in a crucible, about 50 parts by weight of sodium chloride being used as a slag to protect the aluminum from the atmosphere. The aluminum was heated to a temperature of about 1500° C. and about 140 parts by weight of copper added.

35 parts by weight of potassium tantalum fluoride salt were placed in a graphite crucible and a graphite plate placed over the salt. About 150 parts by weight of the solid aluminum-copper alloy were placed on the graphite plate and approximately 50 parts by weight of sodium chloride placed over the aluminum-copper alloy to serve as a protecting slag. The mass was then heated to a temperature of about 1500° C. and the molten aluminum-copper alloy allowed to contact the potassium tantalum fluoride salt. The resulting mass was maintained at a temperature above the melting point of the aluminum-copper alloy for approximately 20 minutes after the alloy became molten to form a reaction mixture. During this period, the mass was agitated with a graphite rod. After cooling, the slag was removed, and the reaction mixture, in the form of an ingot, was treated with dilute nitric acid to dissolve the aluminum-copper alloy. The tantalum was then recovered by filtering the finely divided particles of tantalum from the nitric acid solution, following which the tantalum particles were washed with nitric and hydrochloric acids, washed free of these acids with water, and then dried.

Example 2

Tantalum was produced in the same manner as in Example 1, except that silver was employed instead of copper in the alloy. The results were substantially the same as in Example 1.

Example 3

Tantalum was prepared in the same manner as in Example 1, except that gold was employed instead of copper in the alloy. The results were substantially the same as in Example 1.

Example 4

An aluminum-copper alloy was prepared by melting 15 parts by weight of aluminum in a crucible, about 50 parts by weight of sodium chloride being used as a slag to protect the aluminum from the atmosphere. The aluminum was heated to a temperature of about 1500° C. and about 140 parts by weight of copper added.

25 parts by weight of tantalum oxide were placed in a graphite crucible and a graphite plate placed over the oxide. About 150 parts by weight of the solid aluminum-copper alloy were placed on the graphite plate and approximately 50 parts by weight of sodium fluoride placed over the aluminum-copper alloy to serve as a protecting slag. The mass was then heated to a temperature of about 1500° C. and the molten aluminum-copper alloy allowed to contact the tantalum oxide. The resulting mass was maintained at a temperature above the melting point of the aluminum-copper alloy for approximately 20 minutes after the alloy became molten to form a reaction mixture. During this period, the mass was agitated with a graphite rod. After cooling, the slag was removed, and the reaction mixture, in the form of an ingot, was treated with dilute nitric acid to dissolve the aluminum-copper alloy. The tantalum was then recovered by filtering the finely divided particles of tantalum from the nitric acid solution, following which the tantalum particles were washed with nitric and hydrochloric acids, washed free of these acids with water, and then dried.

Examples 5

Tantalum was produced in the same manner as in Example 4 except that silver was employed instead of copper in the alloy. The results were substantially the same as in Example 4.

Example 6

Tantalum was prepared in the same manner as in Example 4 except that gold was employed instead of copper in the alloy. The results were substantially the same as in Example 4.

Example 7

An aluminum-copper alloy was prepared by melting 15 parts by weight of aluminum in a crucible, about 50 parts by weight of sodium chloride being used as a slag to protect the aluminum from the atmosphere. The aluminum was heated to a temperature of about 1500° C. and about 140 parts by weight of copper added.

25 parts by weight of potassium columbium oxyfluoride salt were placed in a graphite crucible and a graphite plate placed over the salt. About 150 parts by weight of the solid aluminum-copper alloy were placed on the graphite plate and about 50 parts by weight of sodium chloride placed over the aluminum-copper alloy to serve as a protecting slag. The mass was then heated to a temperature of about 1500° C. and the molten alloy allowed to contact the potassium columbium oxyfluoride. The resulting mass was maintained at a temperature above the melting point of the aluminum-copper alloy for approximately 20 minutes after the alloy became molten to form a reaction mixture. During this period the mass was agitated with a graphite rod. After cooling, the slag was removed and the reaction mixture, in the form of an ingot, treated with dilute nitric acid to dissolve the aluminum-copper alloy. The columbium was then recovered from the solution by filtering the finely divided particles of columbium from the nitric acid solution, following which the columbium particles were washed with nitric and hydrochloric acids, washed free of these acids with water, and then dried.

Example 8

Columbium was produced in the same manner as in Example 7, except that silver was employed instead of copper in the alloy. The results were substantially the same as in Example 7.

Example 9

Columbium was produced in the same manner as in Example 7, except that gold was employed instead of copper in the alloy. The results were substantially the same as in Example 7.

Example 10

An aluminum-copper alloy was prepared by melting 15 parts by weight of aluminum in a crucible, about 50 parts by weight of sodium chloride being used as a slag to protect the aluminum from the atmosphere. The aluminum was heated to a temperature of about 1500° C. and about 140 parts by weight of copper added.

18 parts by weight of columbium oxide were placed in a graphite crucible and a graphite plate placed over the oxide. About 150 parts by weight of the solid aluminum-copper alloy were placed on the graphite plate and about 50 parts by weight of potassium fluoride placed over the aluminum-copper alloy to serve as a protecting slag. The mass was then heated to a temperature of about 1500° C. and the molten alloy allowed to contact the columbium oxide. The resulting mass was maintained at a temperature above the melting point of the aluminum-copper alloy for approximately 20 minutes after the alloy became molten to form a reaction mixture. During this period the mass was agitated with a graphite rod. After cooling, the slag was removed and the reaction mixture, in the form of an ingot, treated with dilute nitric acid to dissolve the aluminum-copper alloy. The columbium was then recovered from the solution by filtering the finely divided particles of columbium from the nitric acid solution, following which the columbium particles were washed with nitric and hydrochloric acids, washed free of these acids with water, and then dried.

Example 11

Columbium was produced in the same manner as in Example 10, except that silver was employed instead of copper in the alloy. The results were substantially the same as in Example 10.

Example 12

Columbium was produced in the same manner as in Example 10, except that gold was employed instead of copper in the alloy. The results were substantially the same as in Example 10.

The foregoing detailed description is given for clearness of understanding only, and no unnecessary limitation should be understood therefrom, for some modification will be obvious to those skilled in the art.

We claim:

1. In the recovery of a metal selected from the group consisting of tantalum and columbium, the method which comprises: heating an inorganic compound of the selected metal with an alloy of aluminum including a third metal, said compound being substantially completely reducible to the metal state in molten aluminum, said third metal being present in a sufficient quantity to dissolve substantially all of the aluminum and being incapable of dissolving the selected metal and having a lower melting point than the selected metal, to form a reaction mixture including said selected metal in a finely divided, substantially pure state; and separating the selected metal from the mixture.

2. The method as set forth in claim 1 wherein an excess of an alloy of aluminum and the third metal is employed.

3. In the recovery of a metal selected from the group consisting of tantalum and columbium, the method which comprises: heating an inorganic compound of the selected metal with an alloy of aluminum including a third metal, said compound being substantially completely reducible to the metal state in molten aluminum, said third metal being present in a sufficient quantity to dissolve substantially all of the aluminum and being incapable of dissolving the selected metal, to form a reaction mixture including said selected metal in a finely divided, substantially pure state, said third metal being a member of the class consisting of copper, silver and gold; and separating the selected metal from the mixture.

4. The method of recovering a metal selected from the group consisting of tantalum and columbium from a double fluoride of an alkali metal and the selected metal which comprises: heating a double fluoride of an alkali metal and the selected metal with an alloy of aluminum including a sufficient quantity of a third metal to dissolve substantially all of the aluminum, said third metal being incapable of dissolving the selected metal and having a lower melting point than the selected metal, to form a reaction mixture including the said selected metal in a finely divided, substantially pure state; and separating the selected metal from the mixture, said double fluoride being substantially completely reducible to the metal state in molten aluminum.

5. The method as set forth in claim 4 wherein an excess of the aluminum-third metal alloy is employed.

6. The method of recovering a metal selected from the group consisting of tantalum and columbium from a double fluoride of an alkali metal and the selected metal, which comprises: heating a double fluoride of an alkali metal and the selected metal with an alloy of aluminum including a sufficient quantity of a third metal to dissolve substantially all of the aluminum, said third metal being incapable of dissolving the selected metal, to form a reaction mixture including the said selected metal in a finely divided, substantially pure state, said third metal being a member of the class consisting of copper, silver and gold; and separating the selected metal from the mixture, said double fluoride being substantially completely reducible to the metal state in molten aluminum.

7. The method of recovering a metal selected from the group consisting of tantalum and columbium from a double fluoride of an alkali metal and the selected metal which comprises: heating a double fluoride of an alkali metal and the selected metal with an alloy of aluminum including a sufficient quantity of copper to dissolve substantially all of the aluminum, to form a mixture including the selected metal in a finely divided, substantially pure state; and separating the selected metal in its pure state from the mixture, said double fluoride being substantially completely reducible to the metal state in molten aluminum.

8. The method as set forth in claim 7 wherein the selected metal is tantalum.

9. The method as set forth in claim 7 wherein the selected metal is columbium.

10. The method as set forth in claim 7, wherein the alkali metal is potassium.

11. The method as set forth in claim 10, wherein the selected metal is tantalum.

12. The method as set forth in claim 10, wherein the selected metal is columbium.

13. In the recovery of a metal selected from the group consisting of tantalum and columbium, the method which comprises: heating an oxide of the selected metal with an alloy of aluminum including a third metal, said third metal being present in a sufficient quantity to dissolve substantially all of the aluminum and being incapable of dissolving the selected metal and having a lower melting point than the selected metal, to form a reaction mixture including said selected metal in a finely divided, substantially pure state; and separating the selected metal from the mixture, said oxide being substantially completely reducible to the metal state in molten aluminum.

14. In the recovery of a metal selected from the group consisting of tantalum and columbium, the method which comprises: heating an oxide of the selected metal with an alloy of aluminum including a sufficient quantity of a third metal to dissolve substantially all of the aluminum, said third metal being incapable of dissolving the selected metal, to form a reaction mixture including said selected metal in a finely divided, substantially pure state, said third metal being a member of the class consisting of copper, silver and gold; and separating the selected metal from the mixture said oxide being substantially completely reducible to the metal state in molten aluminum.

15. The method as set forth in claim 13 wherein an excess of an alloy of aluminum and the third metal is employed.

16. The method as set forth in claim 13 wherein the selected metal is tantalum.

17. The method as set forth in claim 13 wherein the selected metal is columbium.

18. The method as set forth in claim 14 wherein the selected metal is tantalum.

19. The method as set forth in claim 14 wherein the selected metal is columbium.

20. In the recovery of a metal selected from the group consisting of tantalum and columbium, the method which comprises: melting an inorganic compound of the selected metal, the compound being substantially completely reducible to the metal state in molten aluminum; adding an alloy of aluminum including a third metal to the molten compound of the selected metal, said third metal being capable of dissolving aluminum and present in a sufficient quantity to dissolve substantially all of the aluminum and being incapable of dissolving the selected metal and having a lower melting point than the selected metal, to form a reaction mixture including said selected metal in a finely divided, substantially pure state; and separating the selected metal from the mixture.

References Cited in the file of this patent

UNITED STATES PATENTS

324,659	Cowles et al.	Aug. 18, 1885
1,022,599	Rossi	Apr. 9, 1912
1,042,694	Ladoff	Oct. 29, 1912
1,321,684	Turner et al.	Nov. 11, 1919
1,373,038	Weber	Mar. 29, 1921
1,644,000	Shumaker	Oct. 4, 1927
1,648,954	Marden	Nov. 5, 1927
2,030,357	Doom	Feb. 11, 1936
2,031,486	Kirsebom	Feb. 18, 1936
2,183,517	Leemans	Dec. 12, 1939
2,205,854	Kroll	June 25, 1940
2,239,277	Stroup	Apr. 22, 1941
2,241,514	Jaeger et al.	May 13, 1941
2,296,196	Behr	Sept. 15, 1942
2,516,863	Gardener	Aug. 1, 1950

FOREIGN PATENTS

536,258	Great Britain	May 8, 1941

OTHER REFERENCES

Kroll: Metal Industry, October 22, 1948, pp. 323–325.

Hansen: Aufbau der Zweistofflegierungen, by Edwards Bros., Inc., Ann Arbor, Mich., 1943, pp. 1–3, 103, 264 and 650.