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METHOD OF RECOVERING REFRACTORY METALS

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This invention relates to a method of recovering metals from their ores and particularly refractory metals, such as tantalum, columbium, tungsten, molybdenum, and the like.

This application is a continuation-in-part of our co-pending United States patent applications Serial Number 534,609, filed September 15, 1955, now abandoned; Serial Number 195,910, filed November 15, 1950, now abandoned; and Serial Number 239,391, filed July 30, 1951, now abandoned.

The new method of this invention permits economical preparation of certain metals for industrial use, which metals heretofore have been difficult to extract from salts or other chemical compounds of these metals. In the specification such a metal will be referred to as the "metal in preparation."

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 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. Potassium carbonate is then added to form the double salts, potassium tantalum fluoride and potassium columbium oxyfluoride. The hot solution is then cooled. The potassium tantalum fluoride crystallizes out leaving the potassium columbium oxyfluoride in solution. The crystallized tantalum salt is separated from the solution, washed and dried and the columbium salt is recovered from the solution. 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 a hydrated oxide ($Ta_2O_5 \cdot H_2O$).

When the pure tantalum and columbium metals are obtained by electrolysis, the metal becomes 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.

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Essentially, the new method of this invention comprises reacting a salt or oxide or other chemical compound of the metal in preparation (A) with a second metal (B), such as, for example, aluminum, to form an intermetallic compound or alloy of the metal in preparation (A) with the second metal (B), the second metal (B) being capable of alloying with another different metal, a third metal (C) such as, for example, copper, silver or gold, in which the metal in preparation (A) is substantially insoluble.

Following the formation of the intermetallic compound or alloy of metal A with metal B, the intermetallic compound or alloy is then reacted with the metal C whereby metal B alloys with the metal C, such as, for example copper, silver or gold, in which metal A (the metal in preparation) is substantially insoluble, the metal A also being insoluble in the alloy of metals B and C. This results in a mixture of metal A in the form of substantially pure, undissolved powder and an alloy of metal B with metal C.

Metal A is then separated from the mixture. This can be achieved, for example, by placing the mixture in an acid in which metal A is substantially insoluble and the alloy of metal B with metal C dissolves. In the event that metal A is columbium or tantalum, hydrochloric, or nitric, or sulphuric acid or a mixture of these acids may be used. After the alloy dissolves, the metal A (the metal in preparation) is then separated from the resulting solution by any suitable procedure well known to persons skilled in the art.

Following is a detailed description of our new method with reference specifically to the preparation of tantalum and columbium. It is to be understood that the new method is applicable to other metals, and particularly other refractory metals, such as molybdenum, tungsten, and the like.

The ore containing tantalum and columbium is converted into the double salts—potassium tantalum fluoride and potassium columbium oxyfluoride or converted into the oxides in accordance with the conventional method described above.

The tantalum or columbium is recovered from its double salt or oxide by combining the double salt or oxide with aluminum to form an intermetallic compound or alloy of aluminum and tantalum or columbium. This intermetallic compound or alloy is then treated with a third and different metal, such as copper, silver or gold, which will alloy with the aluminum but in which the tantalum or columbium is substantially insoluble. The aluminum-tantalum alloy or the aluminum-columbium alloy may be recovered and purified and subsequently treated with the third metal, or the mass resulting from the reduction of the double salt or oxide with aluminum may be treated directly with the third metal. There is an advantage in recovering the aluminum-tantalum or aluminum-columbium alloy prior to the treatment with the third metal, such as copper, silver or gold, in that the alloy may be purified to some extent. On the other hand, the alternative method mentioned above may be employed to effect certain economies in the power required for heating.

In accordance with the method of this invention the tantalum is recovered from the potassium tantalum fluoride by reacting the double salt, potassium tantalum fluoride, with aluminum. This is accomplished by melting preferably an excess quantity of aluminum in a suitable crucible or container, for example a graphite crucible, and slowly adding the potassium tantalum fluoride to the molten aluminum. It is preferred to agitate the molten mass so as to insure contact of all the tantalum salt with the molten aluminum. The reaction between the salt

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and molten aluminum is exothermic and no external heat is required during the course of the addition of the tantalum salt to the molten aluminum. As a result of this reaction, an aluminum-tantalum intermetallic compound or alloy is formed as well as potassium fluoride and aluminum fluoride. These fluorides form a slag which is substantially free of tantalum but which does remove certain impurities associated with the potassium tantalum fluoride salt. This reaction is represented by the following equation:



The efficiency of this reaction with respect to the recovery of tantalum exceeds 90% in most instances. This step in the recovery method may be illustrated by the following specific example:

Example 1

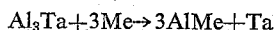
3400 parts by weight of aluminum in the form of pellets or shot were melted in a graphite crucible and heated to approximately 1000° C. 5000 parts by weight of potassium tantalum fluoride were added in 400 part lots over a period of about 30 minutes, the melt being stirred with a graphite rod after each addition of the potassium tantalum fluoride. No external heat is required during this period because of the heat resulting from the reaction.

After all of the fluoride had been added, the melt was maintained at a temperature of between 1000° C. and about 1450° C. for about 1 hour, being agitated at 15 minute intervals. The slag was removed and about 1600 parts by weight of potassium chloride added. The heating continued for about 15 minutes. During this period the molten mass was agitated so as to remove the residual slag from the molten metal.

The molten potassium chloride was then removed and the metallic mass allowed to solidify and cool. The free aluminum in the ingot was dissolved with a hydrochloric acid solution and the resulting aluminum-tantalum alloy or compound in the form of powder was washed free of acid, dried and screened. The yield was approximately 94%.

The aluminum-tantalum alloy or compound, as noted above corresponds to an intermetallic compound or alloy which we believe has the formula Al_3Ta even though an excess of aluminum is employed. The tantalum cannot be recovered from this alloy by removal of the aluminum as by treatment with acids or by heating the material in a high vacuum to vaporize the aluminum.

We have discovered that the aluminum and tantalum may be separated from the aluminum-tantalum intermetallic compound or alloy by treating it with a third and different metal which alloys with aluminum and in which the tantalum is substantially insoluble, such as copper, silver or gold. It is preferred that such third metal have a low melting point. These third metals selectively dissolve the aluminum to form an alloy with the aluminum, and the tantalum, being substantially insoluble in the alloy, becomes dispersed as minute grains or crystals throughout the body of the alloy. The alloy is then dissolved by means of a suitable acid solution in which the tantalum is substantially insoluble or by other means, and the tantalum is recovered in the form of tantalum crystals or powder. This reaction may be illustrated by the following equation in which Me represents the third metal:



The aluminum-tantalum intermetallic compound or alloy is in the form of fine powder and may be employed in such form for the recovery of the tantalum. However, for large scale operation it is preferably pressed into pellets to simplify its addition to the molten copper. The aluminum-tantalum intermetallic compound or alloy is exceedingly difficult to press by itself to form a self-supporting body and we have found that satisfactory pellets may be prepared by adding a portion of the third metal

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in the form of flake or powder to the aluminum-tantalum intermetallic compound or alloy powder and pressing the mixture. Such pressed bodies are slowly added to a molten mass of the third metal, which is preferably covered by a low melting flux or slag, such as sodium chloride, potassium chloride, magnesium chloride or a mixture of these chlorides, to protect the mass, particularly the tantalum, from the atmosphere. In this reaction it is preferred to employ an excess of the third metal so as to insure a more complete recovery of the tantalum. We have found that a ratio by weight of the aluminum-tantalum intermetallic compound or alloy to the third metal of about 1:4 is satisfactory. After the reaction is complete and the mass has cooled, it is removed from the crucible. Most of the slag remaining on the surface of the ingot is removed mechanically and the balance is removed by dissolving in water. The ingot is then immersed first in nitric acid and then hydrochloric acid to dissolve the aluminum-third metal alloy. The tantalum powder is then washed free of acids and dried.

In order to specifically illustrate this step in the method, the step is illustrated by reference to the separation of aluminum and tantalum or the recovery of the tantalum from the aluminum-tantalum intermetallic compound or alloy by the use of copper. This specific example is described since copper is relatively inexpensive and is readily recoverable for re-use in the process.

Example 2

3400 parts by weight of aluminum in the form of pellets or shot were melted in a graphite crucible and heated to approximately 1000° C. 3000 parts by weight of tantalum oxide (Ta_2O_5) and 2000 parts by weight of potassium fluoride (KF), a flux, were mixed. The mixture was added in 400 part lots over a period of about 30 minutes, to the molten aluminum. The melt was stirred with a graphite rod after each addition of the tantalum oxide and potassium fluoride mixture. No external heat is required during this period because of the heat resulting from the reaction.

After all of the mixture had been added, the melt was maintained at a temperature of between 1000° C. and about 1450° C. for about 1 hour, being agitated at 15 minute intervals. The slag was removed and about 1600 parts by weight of potassium chloride added. The heating was continued for about 15 minutes. During this period the molten mass was agitated so as to remove the residual slag from the molten metal.

The molten potassium chloride was then removed and the metallic mass allowed to solidify and cool. The free aluminum in the ingot was dissolved with a hydrochloric acid solution and the resulting aluminum-tantalum alloy or compound in the form of powder was washed free of acid, dried and screened. The yield was approximately 94%.

The aluminum and tantalum were separated in the same manner as in Example 1. The intermetallic compound or alloy resulting from reduction of the tantalum oxide with aluminum in this example is the same as the aluminum-tantalum intermetallic compound or alloy which resulted from reduction of the tantalum salt utilized in Example 1.

In this example potassium fluoride was used with the tantalum oxide as a flux to promote the reaction between the tantalum oxide and the aluminum. It should be understood that any alkali metal halide flux may be substituted for the potassium fluoride. It has been found that the fluorides are preferred, however, because of their high solubility and low volatility.

In accordance with this invention, it has been found that the oxides of the refractory metals, as well as other compounds thereof, when mixed with appropriate flux as described here and above, may be used in the process of this invention for the recovery of the refractory metal by forming an intermetallic compound or alloy thereof

with a second metal such as aluminum that readily alloys with a third metal such as copper, silver or gold in which the refractory metal is insoluble.

Example 3

3000 parts by weight of powdered aluminum-tantalum intermetallic compound or alloy and 1000 parts by weight of flake copper were mixed and pressed into bars approximately 6 inches in length and 1/4 inch square. 11,000 parts by weight of copper pellets were melted in a graphite crucible and potassium chloride added to form a protective slag. The copper was heated to about 1180° C., and the pressed bars containing the aluminum-tantalum intermetallic compound or alloy were introduced at intervals into the molten copper over a period of about 2 hours and the mass was maintained at the elevated temperature for an additional 1/2 hour.

After cooling, the ingot was immersed in nitric acid. The aluminum-copper alloy dissolved and the undissolved tantalum powder was washed free of acid and dried. Approximately 1935 parts by weight of tantalum were recovered showing an efficiency of approximately 93.5%.

Similar results were obtained when employing silver and gold in place of copper in the above example.

As pointed out above, tantalum and columbium may be recovered by reacting with aluminum and treating the molten mass with the third metal without first recovering the aluminum-tantalum or aluminum-columbium intermetallic compounds or alloys and subsequently heating and treating with the third metal. By the use of this single heating step it is not necessary to perform the steps required for the recovery of the aluminum-tantalum intermetallic compound or alloy, and subsequently reheat it.

This one step recovery may be illustrated by the following specific example:

Example 4

1500 parts by weight of aluminum were melted in a graphite crucible and heated to about 1080° C. 3000 parts by weight of potassium tantalum fluoride were added slowly, the melt being stirred with a graphite rod after each addition of the tantalum salt. After all of the tantalum salt had been added, the mass was maintained at about 1080° C. for 30 minutes, after which the slag was removed and replaced by about 100 parts by weight of potassium chloride which was removed after about 15 minutes to remove the residual slag. 1500 parts by weight of sodium chloride were then added. About 15,000 parts by weight of copper were added and the temperature of the mass maintained at about 1100° C. for about 1 1/4 hours, being stirred several times with a graphite rod. The mass was then allowed to cool, the protecting sodium chloride salt removed, and the ingot immersed in nitric acid. The aluminum-copper alloy dissolved in the acid and the tantalum residue was washed free of acid and dried. The yield of tantalum was about 1350 parts by weight, showing an efficiency of about 97%.

Example 5

Example 4 was repeated using a mixture of 1800 parts by weight of tantalum oxide and 1200 parts by weight of potassium fluoride in place of potassium tantalum fluoride. The results were substantially the same as the results of Example 4.

Similar results were obtained when employing silver and gold in place of copper in Examples 4 and 5 above.

Tests similar to those set forth in Examples 1-5 inclusive were repeated, except that potassium columbium oxyfluoride was used in place of potassium tantalum fluoride, and columbium oxide (Cb_2O_5) in place of tantalum oxide, the ratio of potassium columbium oxyfluoride or the mixture of columbium oxide and potassium fluoride, to aluminum being 1:1. The results were satisfactory.

The foregoing detailed description has been given for

clarification of understanding only, and no unnecessary limitations should be understood therefrom, for some modification will be obvious to those skilled in the art.

We claim:

1. In the preparation of a metal for industrial use, the method comprising the following steps in the order stated: reacting with aluminum, an inorganic compound of a first metal (being the metal in preparation) selected from the class consisting of tantalum, columbium, tungsten and molybdenum, which compound is substantially completely reducible by aluminum to the metallic state, to form an alloy of said first metal with aluminum, adding the alloy to a molten mass of a low melting point third metal capable of dissolving the aluminum of the alloy and incapable of dissolving the selected metal, to form a mixture of an alloy of said third metal with said aluminum and of the said first metal in a free state, said first metal being insoluble in said alloy of said third metal with aluminum, and separating said first metal in a free state from the alloy of said third metal with said aluminum.

2. In the preparation of a metal for industrial use, the method comprising the following steps in the order stated: reacting with aluminum, an inorganic compound of a first metal (being the metal in preparation) selected from the class consisting of tantalum, columbium, tungsten and molybdenum, which compound is substantially completely reducible by aluminum to the metallic state, to form an alloy of said first metal with aluminum; adding the said alloy to a molten mass of a third metal selected from the class consisting of copper, silver and gold capable of dissolving the aluminum of the alloy and incapable of dissolving the selected metal, to form a mixture of an alloy of said third metal with aluminum and of the said first metal in a free state; and separating said first metal in a free state from the alloy of said third metal and aluminum.

3. In the preparation of tantalum for industrial use, the method comprising the following steps in the order stated: reacting with aluminum, an inorganic compound of tantalum which compound is substantially completely reducible by aluminum to the metallic state, to form an alloy of tantalum and aluminum; adding the said alloy to a molten mass of copper which is capable of dissolving the aluminum of the alloy and incapable of dissolving the tantalum, to form a mixture of a copper-aluminum alloy and tantalum in a free state; and separating the tantalum from the copper-aluminum alloy.

4. In the preparation of columbium for industrial use, the method comprising the following steps in the order stated: reacting with aluminum, an inorganic compound of columbium which compound is substantially completely reducible by aluminum to the metallic state, to form an alloy of columbium and aluminum; adding the said alloy to a molten mass of copper which is capable of dissolving the aluminum of the alloy and incapable of dissolving the columbium to form a mixture of a copper-aluminum alloy and columbium in a free state; and separating the columbium from the copper-aluminum alloy.

5. In the preparation of a metal for industrial use, the method comprising the following steps in the order stated: reacting an oxide of a first metal (being the metal in preparation) selected from the class consisting of tantalum, columbium, tungsten and molybdenum, with aluminum to form an alloy of said first metal with aluminum, said oxide being substantially completely reducible by aluminum to the metallic state, adding the alloy to a molten mass of a low melting point third metal which is capable of dissolving the aluminum of the alloy and incapable of dissolving the selected metal, to form a mixture of an alloy of said third metal with said aluminum and of the said first metal in a free state, said first metal being insoluble in said alloy of said third metal with aluminum, and separating said first metal in a free

state from the alloy of said third metal with said aluminum.

6. In the preparation of a metal for industrial use, the method comprising the following steps in the order stated: reacting an oxide of a first metal (being the metal in preparation) selected from the class consisting of tantalum, columbium, tungsten and molybdenum with aluminum to form an alloy of said first metal with aluminum, said oxide being substantially completely reducible by aluminum to the metallic state; adding the said alloy to a molten mass of a third metal selected from the class consisting of copper, silver and gold which is capable of dissolving the aluminum of the alloy and incapable of dissolving the selected metal to form a mixture of an alloy of said third metal with aluminum and of the said first metal in a free state; and separating said first metal in a free state from the alloy of said third metal and aluminum.

7. In the preparation of tantalum for industrial use, the method comprising the following steps in the order stated: reacting an oxide of tantalum with aluminum to form an alloy, said oxide being substantially completely reducible by aluminum to the metallic state; adding the said alloy to a molten mass of copper which is capable of dissolving the aluminum of the alloy and incapable of dissolving the tantalum, to form a mixture of a copper-aluminum alloy and tantalum in a free state; and separating the tantalum from the copper-aluminum alloy.

8. In the preparation of columbium for industrial use, the method comprising the following steps in the order stated: reacting an oxide of columbium with aluminum to form an alloy, said oxide being substantially completely reducible by aluminum to the metallic state; adding the said alloy to a molten mass of copper which is capable of dissolving the aluminum of the alloy and incapable of dissolving the columbium to form a mixture of a copper-aluminum alloy and columbium in a free state; and separating the columbium from the copper-aluminum alloy.

9. In the preparation of a metal for industrial use, the method comprising the following steps in the order stated: reacting an alkali metal halide salt of a first metal (being the metal in preparation) selected from the class consisting of tantalum, columbium, tungsten and molybdenum, with aluminum to form an alloy of said first metal with aluminum, said alkali metal halide salt being substantially completely reducible by aluminum to the metallic state, adding the alloy to a molten mass of a low melting point third metal which is capable of dissolving the aluminum of the alloy and incapable of dissolving the selected metal, to form a mixture of an alloy of said third metal with said aluminum and of the said first metal in a free state, said first metal being insoluble in said alloy of said third metal with aluminum, and separating said first metal in a free state from the alloy of said third metal with said aluminum.

10. In the preparation of a metal for industrial use, the method comprising the following steps in the order stated: reacting an alkali metal halide salt of a first metal (being the metal in preparation) selected from the class consisting of tantalum, columbium, tungsten and molybdenum with aluminum to form an alloy of said first metal with aluminum, said alkali metal halide salt being substantially completely reducible by aluminum to the metallic state; adding the said alloy to a molten mass of a third metal selected from the class consisting of copper, silver and gold which is capable of dissolving the aluminum of the alloy and incapable of dissolving the selected metal, to form a mixture of an alloy of said third metal with aluminum and of the said first metal in a free state; and separating said first metal in a free state from the alloy of said third metal and aluminum.

11. In the preparation of tantalum for industrial use, the method comprising the following steps in the order

stated: reacting an alkali metal halide salt of tantalum with aluminum to form an alloy, said alkali metal halide salt being substantially completely reducible by aluminum to the metallic state; adding the said alloy to a molten mass of copper which is capable of dissolving the aluminum of the alloy and incapable of dissolving the tantalum, to form a mixture of a copper-aluminum alloy and tantalum in a free state; and separating the tantalum from the copper-aluminum alloy.

12. In the preparation of columbium for industrial use, the method comprising the following steps in the order stated: reacting an alkali metal halide salt of columbium with aluminum to form an alloy, said alkali metal halide salt being substantially completely reducible by aluminum to the metallic state; adding the said alloy to a molten mass of copper which is capable of dissolving the aluminum of the alloy and incapable of dissolving the columbium, to form a mixture of a copper-aluminum alloy and columbium in a free state; and separating the columbium from the copper-aluminum alloy.

13. The method of separating a metal selected from the group consisting of tantalum, tungsten, molybdenum and columbium from an alloy of the selected metal and aluminum, comprising: adding the said alloy to a molten mass of low melting point third metal capable of dissolving the aluminum of the alloy and of forming an alloy with the aluminum and in which the selected metal is substantially insoluble to form an alloy of the aluminum and the third metal; and separating the selected metal from the said aluminum-third metal alloy.

14. The method of separating tantalum from an alloy of tantalum and aluminum, comprising: adding the alloy of tantalum and aluminum to a molten mass of low melting point third metal capable of dissolving aluminum of the alloy and of forming an alloy with the aluminum and in which the tantalum is substantially insoluble, to form an alloy of the aluminum and the said third metal; and separating the tantalum from the said aluminum-third metal alloy.

15. The method of separating tantalum from an alloy of tantalum and aluminum, comprising: adding the alloy of tantalum and aluminum to a molten mass of copper which is capable of dissolving the aluminum of the alloy and in which the tantalum is substantially insoluble, to form an alloy of the aluminum and copper; and separating the tantalum from the aluminum-copper alloy.

16. The method of separating columbium from an alloy of columbium and aluminum, comprising: adding the alloy of columbium and aluminum to a molten mass of a low melting point third metal capable of dissolving the aluminum of the alloy and of forming an alloy with the aluminum and in which the columbium is substantially insoluble, to form an alloy of the aluminum and the said third metal; and separating the columbium from the said aluminum-third metal alloy.

17. The method of separating columbium from an alloy of columbium and aluminum, comprising: adding the alloy of columbium and aluminum to a molten mass of copper which is capable of dissolving the aluminum of the alloy and in which the columbium is substantially insoluble, to form an alloy of the aluminum and copper; and separating the columbium from the aluminum-copper alloy.

18. The method of separating a metal selected from the group consisting of tantalum, tungsten, molybdenum and columbium from an alloy of the selected metal and aluminum, comprising: adding the said selected metal-aluminum alloy to a molten mass of a third metal which is capable of dissolving the aluminum of the alloy and which is selected from the group consisting of copper, silver and gold, which is capable of dissolving the aluminum of the alloy and in which the selected metal is substantially insoluble, to form an alloy of the aluminum and the third metal; and separating the first named, selected metal from the aluminum-third metal alloy.

23. The method of recovering tantalum from a double fluoride of potassium and tantalum, said double fluoride of potassium being substantially completely reducible by aluminum to the metallic state, which comprises: heating the double fluoride of potassium and tantalum with an excess of aluminum to form an alloy of aluminum and tantalum; then heating the aluminum-tantalum alloy with the copper which is capable of dissolving the aluminum of the alloy and in which the tantalum is substantially insoluble, to form an alloy of the aluminum and the copper, thereby producing tantalum in a finely

29. The method of recovering columbium from an oxide of columbium, said oxide being substantially completely reducible by aluminum to the metallic state, which comprises: heating the oxide of columbium with an excess

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of aluminum to form an alloy of aluminum and columbium; then heating the aluminum-columbium alloy with copper which is capable of dissolving the aluminum of the alloy and in which the columbium is substantially insoluble, to form an alloy of the aluminum and the copper, thereby producing columbium in a finely divided state; and separating the columbium from the aluminum-copper alloy.

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