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METALLIC COLUMBIUM AND PROCESS FOR MAKING THE SAME

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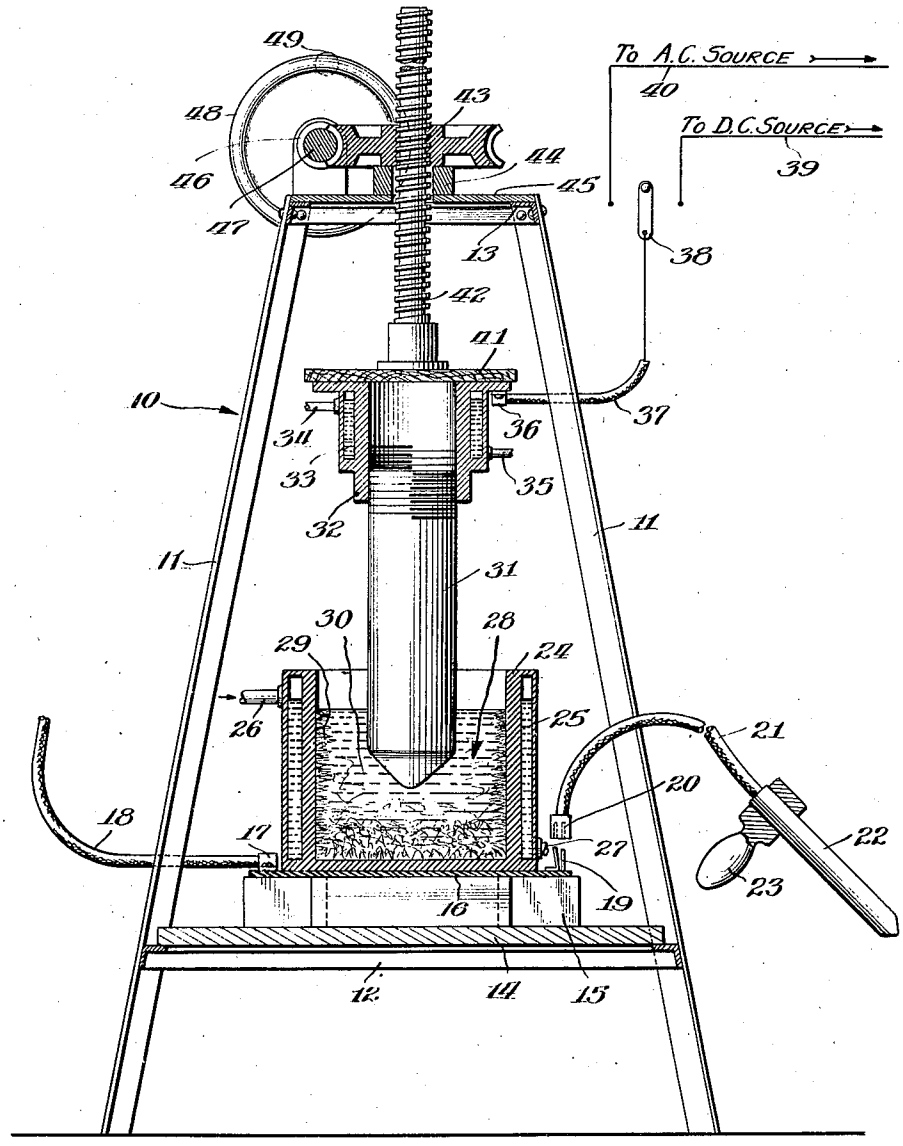


Fig. 1.

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METALLIC COLUMBIUM AND PROCESS FOR MAKING THE SAME

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This invention relates to a metallurgical process and the resulting product and it pertains more specifically to metallic columbium (niobium) and the method and means of producing it.

Columbium is closely associated with tantalum in its occurrence and in its general physical and chemical properties, tantalite and columbite ores being its chief sources. The electrolytic process for the production of metallic tantalum has, however, been found to be ineffectual to produce columbium. Heretofore only a few grams of the metal have ever been produced and the metal has not been available commercially. In fact, prior to my invention the metal has never been prepared in sufficient quantity and of sufficient purity to accurately determine its physical and chemical qualities and constants. The object of this invention is to prepare pure metallic columbium in workable quantities.

A further object is to prepare pure columbium sheets, rods, wires, apparatus, etc.

A further object is to provide an improved process for working columbium bearing ores, removing impurities, and preparing a columbium bearing compound that is suitable for the electrolytic production of metallic columbium.

A further object is to provide an electrolytic process for reducing the columbium compound to pure metallic columbium.

A further object is to provide a process for separating the purified metallic columbium from its flux and for making it into rods, sheets, wires, etc.

A further object is to provide an improved apparatus for carrying out the above process steps and for manipulating said apparatus.

Other objects will be apparent as the detailed description of my invention proceeds.

My invention may be briefly outlined as follows:

Columbite ore or other columbium bearing material is fused with potassium hydroxide (KOH) to give potassium columbate. The potassium columbate and other soluble salts are leached out of the fused material, filtered and converted to di-potassium salts, including di-potassium columbium oxy-fluoride (K_2CbOF_5). This salt is freed from tungsten, tin and other impurities, dried, and placed in an iron vessel (cathode) provided with a water-cooled jacket and connected to a source of both alternating current and direct current. A carbon anode is introduced in the salt, fusion of the salt is accomplished by an auxiliary arc device, and when the entire mass of salt is fused the direct current is turned on and the voltage is carefully regulated by varying the position of the electrodes. This process carried on as hereafter described results in the deposit of relatively large crystals of pure metallic columbium. These are separated from the slag or flux by washing and all impurities are removed by suitable treatment with acid and alkalies. The dried and purified crystals are compressed to form a bar which is sintered or fused in a vacuum until the crystals combine to form a rod which may be swaged and drawn into wires or rolled into sheets.

To enable those skilled in the art to better understand and practice the invention, I will now give a detailed description of a specific embodiment of my invention, it being understood that this is illustrative only and that the scope of the invention is to be limited only by the appended claims.

The drawing Fig. 1 which forms a part of this specification shows a vertical section partly diagrammatic of the electrolytic apparatus used in this process.

The first step in this process is the fusion of the ore with potassium hydroxide. The term ore as used herein includes all columbium bearing materials such as natural ore deposits, slags, by-products, etc. This ore is finely ground and mixed with an equivalent amount of potassium hydroxide in an iron crucible and is fused to red heat, preferably in a gas furnace. The fusion is carried on until all of the columbium is converted to potassium columbate. When this reaction is completed, the mass is cooled, pulverized and leached to remove the soluble

columbates, tantalates, stannates, tungstates, etc.

The clear filtrate is then acidified with hydrofluoric acid to effect precipitation of the double potassium fluoride of tantalum which is much less soluble than the corresponding columbium salt. After the tantalum salt is removed, the filtrate which contains the columbium salts and impurities is concenerated. The residue from this concentration contains double potassium oxy-fluoride of columbium ($2KF.CbOF_3H_2O$), together with small amounts of tungsten, tin, titanium, etc. Since the difference in solubility of these salts is not as great as that of the columbium from tantalum, the purification of the columbium is much more difficult than in the case of tantalum. I have devised the following procedures for purifying the columbium salt:

A hot solution of potassium columbium oxy-fluoride is poured into a fairly concentrated solution of sodium hydroxide to give a sodium columbate having a formula $7Na_2O.6Cb_2O_5.31H_2O$. This salt is insoluble in water containing free sodium hydroxide and it, therefore, precepitates while the sodium stannate, tungstate, etc., being soluble, will remain in the solution. By washing the crystalline sodium columbate precepitate with water containing sufficient sodium hydroxide the impurities may be removed without dissolving the columbium salt. This material still contains some tantalum.

The separation of the last traces of tantalum from columbium is very difficult. For practical purposes it will not be necessary to remove all of the tantalum as 1% or 2% of it in columbium metal would probably not mitigate against its use for any commercial purpose which may develop. In order to thoroughly remove the tantalum, the sodium columbate crystals are treated with a mineral acid, such as nitric or sulphuric, the resulting columbic acid is washed and then dissolved in dilute hydro-fluoric acid, keeping the solution quite concentrated and adding a small amount of potassium carbonate or hydroxide which, in solution, forms a fluoride which, in turn, will cause a precipitation of most of the tantalum still present, which is filtered out. The double fluoride of columbium which is again obtained by adding a sufficient amount of potassium fluoride is re-crystallized from pure water. This salt is not affected by pure water while K_2TaF_7 decomposes in a water solution unless a small amount of hydro-fluoric acid is present. If, therefore, a double fluoride of columbium containing some tantalum is re-crystallized from pure water there is a tendency for the tantalum to revert to a basic or oxy-fluoride and to gradually precipitate. This tendency can be magnified by thoroughly baking the columbium salt or by a prolonged boiling of the aqueous solution. If this baking process is resorted to between crystallizations, three or four such treatments will give a columbium salt substantially free from tantalum. Another modification would be to actually fuse the columbium double fluoride and then boil the solution of the fused material. This treatment would render the tantalum and probably a little of the columbium insoluble.

From the above process I obtain a substantially pure di-potassium oxy-fluoride of columbium which is suitable for the electrolytic process which follows. It is to be noted that, while there is only one potassium double fluoride of tantalum ($2KF.TaF_5$), there is a great number of potassium double fluorides of columbium such as $3KF.CbOF_3$, $3KF.HF.CbOF_3$, $5KF.3CbOF_3.H_2O$, $4KF.3CbOF_3.H_2O$, $2KF.CbF_5$, and $2KF.CbOF_3.H_2O$. The electrolytic treatment will depend to a certain extent upon the particular salt used. In the following process I will describe the electrolytic reduction of the di-potassium oxy-fluoride.

Electrolytic reduction of the columbium salt

To better understand the electrolytic process, attention is directed to the accompanying drawing showing the apparatus used. A frame 10 composed of four angle iron supports 11 is tied together by angle iron tie members 12 and 13. The tie members 12 support a wooden platform 14 on which are placed bricks 15 for insulating and supporting the copper plate 16. This copper plate is provided with a terminal 17, to which is secured a heavy conductor 18 adapted to carry up to 800 to 1000 amperes. The plate 16 also contains projections 19 adapted to fit in a socket 20 to provide an electrical connection to conductor 21 which is secured to a carbon rod 22, the latter being provided with a suitably insulated handle 23. An iron receptacle 24, preferably about 7″ in diameter and 7″ deep, rests on the copper plate 16 to form electrical contact therewith. This receptacle is provided with a water jacket 25 having an outlet 26 and an inlet 27. The receptacle is adapted to contain the di-potassium oxy-fluoride of columbium 28 prepared as above stated. During the process some of this salt when fused forms a crystalline crust 29 around the sides and as the process is continued a mass of columbium crystals intermixed with slag 30 is deposited in the bottom of the receptacle. The metal receptacle referred to acts as a cathode in the electrical process.

A carbon anode 31, preferably about 3″ in diameter, is mounted to be moved vertically within the frame. It is secured to a metal base 32 which is provided with a cooling water jacket 33 having an inlet 34

and an outlet 35. This base is also provided with a terminal 36 to which is connected a conductor 37 adapted to carry currents up to 1000 amperes. This conductor is connected to a double throw switch 38 which in one position is adapted to connect the apparatus to a direct current source and which in another position connects it to an alternating current source. The base 32 is connected through an insulator block 41 to a screw 42 which is threaded in a tapped aperture in worm gear 43 which rests on a suitable bearing 44 supported by the top 45. The worm gear is driven by a worm 46 keyed on a shaft 47 to which is also keyed a wheel 48 provided with a handle 49.

The di-potassium oxy-fluoride of columbium is thoroughly dried and all of its water of crystallization is driven out of it by heating it in a platinum pan. This step is important because if any water remains in the salt it may cause an explosion in the electrolytic process which follows.

The thoroughly dried salt is placed in the receptacle 24 and the carbon anode 31 is lowered to within the fraction of an inch of the bottom of the iron receptacle. This process is carried on under a hood and at this point the fan is turned on so that any fumes, vapors or gases may be withdrawn without imperiling the health of the operator. The switch 38 is connected to the alternating current source, the plug 20 is secured to the plate 16 and by means of the carbon rod 22 an arc is drawn from the anode 31. The intense heat of the electric arc fuses the salt immediately in the vicinity and the carbon rod is gradually moved further and further from the anode until all of the salt between the cathode 24 and the anode 31 is in a fused condition. As soon as the fused salt reaches the iron cathode it will "take"—that is, the circuit will be closed through the fused salt and the carbon rod 22 may be withdrawn and removed from the apparatus. The alternating current is allowed to continue until all of the salt is fused except the crust which forms around the periphery of the receptacle due to the cooling jacket 25.

In the next step of my process I throw the switch from the alternating current source to the direct current source and pass a direct current of about 400 to 600 amperes at 20 volts through the fused bath. The current density is very important in this process and I have found that the current density used in the production of tantalum is not applicable to the production of columbium. The current density is regulated by maintaining the voltage within proper limits, preferably at 20 volts, and this is effected by raising or lowering the anode by turning the wheel 48. At the beginning of the operation the anode is probably one half an inch from the bottom of the receptacle (cathode) and, as the columbium crystals separate out and become interspersed with the slag on the bottom of the receptacle, it is necessary to gradually raise the anode. The complete process for reducing a charge requires about eight hours.

An obstacle in electrolytic processes of this type is the so-called anode effect, that is, a gassing around the anode which breaks the circuit. In the tantalum process an oxide was added to the fused salt for overcoming this difficulty, the oxygen probably combining with the carbon at the anode and thereby preventing the "anode defect." In the columbium process, by using an oxy-fluoride I am not bothered by the anode effect due to the oxygen content of the salt. During the process, however, oxides or double fluorides of columbium may be added to the fused salt to replenish its columbium content.

When the process is completed the mass is allowed to cool. In cooling its shrinks and is therefore easy to remove from the receptacle.

Treatment of metallic columbium

The mass resulting from the electrolytic process consists of crystals of pure metallic columbium interspersed with crystals of the salt of the electrolysis. This mass is ground, preferably by means of an impact pulverizer, and the bulk of the salt is removed from the metal crystals by means of air separation. Other conventional metallurgical processes may be used for mechanically separating the salt from the metal. When the mechanical separation has been carried as far as practical the crystals of columbium are treated with dilute hydrochloric acid which tends to dissolve the salt and to loosen it from the metal. The crystals are agitated in this solution and subsequently washed with water, the acid if necessary being neutralized with a small amount of potassium hydroxide. It should be noted, however, that potassium hydroxide attacks columbium to a certain extent.

After the crystals or granules of metallic columbium have been freed from the salt, the only remaining impurity is a small amount of carbon which is introduced into the fused bath by the anode during the electrolytic process. The percent of carbon may be determined by any conventional analysis and an amount of columbium oxide may be added to the columbium crystals in sufficient quantity to permit the oxygen to combine with the carbon to form carbon monoxide. The crystals are then compressed into a bar under a pressure of about fifty tons per square inch. This pressure tends to cause the grains to flow together and gives a compact rod which may be readily handled without danger of fracture. The rod is

placed in a vacuum furnace between two electrodes which are secured to its ends and which are adapted to be moved to conform to the length of the rod which shortens as the rod is sintered.

The pumps are then started to remove all gases from the vessel containing the rod, especially nitrogen, hydrogen and oxygen. The pumps are operated continuously throughout the process to discharge the occluded gases which are freed at elevated temperatures and to discharge the carbon monoxide formed in the sintering process. It is essential that these gases be eliminated because their presence in the chamber with the highly heated columbium would cause this metal to form hydrides, nitrides, oxides, etc. and thereby cause the bar to expand and become brittle.

When the pressure in the chamber is reduced to about .005 inch of mercury the electric current is turned on sufficient to elevate the temperature of the bar to a point slightly below its melting point (1900 to 2000° C.). The current required will naturally vary with the size of the rod, a rod $\frac{5}{8}'' \times \frac{1}{2}''$ requiring a current of about 2800 amperes.

Instead of furnishing the oxygen in the form of columbium oxide, I may use magnesium oxide or the oxide of some other metal which is volatile at the temperature to which the bar is heated. When a calculated amount of magnesium oxide is mixed with the granules in such proportions that the oxygen combines with the carbon remaining in the columbium crystals and the rod is compressed and heated as above stated, it will be noted that the vacuum drops when the carbon monoxide is formed, that the vacuum gradually is re-established as the heating continues, and that the magnesium is vaporized and deposited on the walls of the container. This process has proven very effective in the purification of metals such as tantalum, columbium, etc.

The bar is allowed to cool in a vacuum. It is then swaged and drawn into wires or rolled into plates. The metal prepared as above described is more workable than tantalum, is malleable, ductile, and easily handled. Its co-efficient of expansion is about 8×10^{-6}.

This is an extremely important feature because it permits the metal to be fused in glass, the co-efficient of expansion of metal and of glass being practically the same. The metal is therefore in a class with platinum in this respect and is especially adapted for use as elements in vacuum tubes, incandescent light bulbs, etc. The metal has high absorptive qualities at temperatures approaching a red heat and if the elements of a vacuum tube are made of this metal it will absorb the remaining traces of gas in the tube and thereby serve as a continuous "getter". The metal is impervious to all acids except hydro-fluoric acid and is especially useful in the manufacture of chemical apparatus, dental and surgical implements, etc.

While I have described a preferred embodiment of my invention, it is understood that I am not limited to the details given except as defined by the following claims.

I claim:

1. The process of producing metallic columbium which comprises electrolytically reducing a double potassium fluoride of columbium.

2. The process of producing metallic columbium which comprises electrolyzing fused di-potassium, columbium oxy-fluoride.

3. The process of producing metallic columbium which comprises fusing a columbium bearing material with potassium hydroxide, leaching the fused mass, treating the resulting solution with hydro-fluoric acid for removing tantalum, and converting the columbium compound to a sodium columbate to effect a separation from tin and tungsten.

4. The process of producing metallic columbium which comprises fusing a columbium bearing material with potassium hydroxide, dissolving the soluble columbium compound with water, removing the other metals by chemical treatment, converting the columbium into a double potassium fluoride, fusing the double potassium fluoride and passing electric current through the fused salt.

5. The process of producing metallic columbium which comprises fusing the ore with potassium hydroxide, dissolving the soluble salts with water, separating the columbium from other metals by chemical treatments, converting the columbium to a double potassium fluoride, driving out all water of combination from the double potassium fluoride, fusing the anhydrous salt and passing a current through the fused salt.

6. The process of producing metallic columbium which comprises removing the water from a double potassium fluoride of columbium, fusing this salt by an electric arc and passing a direct current through the fused salt at a current density of about 50 to 70 amperes per square inch.

7. The process of producing metallic columbium which comprises placing a dry columbium bearing compound in a cathode, inserting an anode in the compound, drawing an arc from the anode to effect fusion of the salt, whereby it is rendered conductive from the bottom, passing a direct current from the anode to the cathode through the fused compound, and regulating the current density by elevating the anode as crystals are deposited in the bottom to keep the potential at about 20 volts.

8. The process of producing meallic columbium which comprises passing a direct current through a fused double potassium fluoride of columbium, maintaining the current density at about 50 to 70 amperes per square inch by keeping the potential of the direct current at about 20 volts, mechanically separating the crystals of columbium thus formed from the remaining slag, adding a metallic oxide for removing carbon impurities, compressing the crystals with the oxide to form a bar and sintering the bar in a substantial vacuum.

In witness whereof, I hereunto subscribed my name this 17th day of January, 1928.

CLARENCE W. BALKE.