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PRODUCTION OF COLUMBIUM AND TANTALUM

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The present invention relates to a process for the production of columbium and/or tantalum and, more particularly, to a single-step, solid-phase process for the production of pure columbium and/or tantalum.

The principal processes by which columbium and tantalum are presently prepared are by electrolytic deposition from a fused salt bath, by reduction of the reactive metal halide with an alkali metal or other reducing metals such as magnesium, aluminum or zinc, or by an oxide-carbide reaction.

In practicing the first two above-mentioned processes, the highly reactive liquid materials that are employed must be amply protected before, during and even after the reaction. Where columbium and tantalum are produced by electrolysis, the cathodic deposits are immersed in the electrolyte throughout the process and, therefore, a further cleaning of the product is necessary when it is removed from the salt bath, such cleaning is usually accomplished by acid leaching.

In reduction of the reactive metal halide, the resulting metal is intermingled with salt products of the reaction and must be separated either by leaching in an aqueous solution, in which case impurities may be picked up, or by vacuum distillation, which is a very expensive procedure. In some instances, operating conditions for both processes are sufficiently difficult that metals of consistently high purity may not always be produced.

Another serious drawback attendant with production of the metals in question, either by electrolysis or by the reduction of reactive metal halides, is the inability to scale production up to major commercial proportions since there is a practical limit to the size to which an electrolytic cell or other reaction chamber may be increased. Still another disadvantage in the latter process is the fact that the materials are reacted in the liquid phase. This increases the possibility of picking up impurities in the reaction chamber.

The production of either columbium or tantalum by the oxide-carbide reaction necessarily involves a two-step operation since a pure carbide must first be produced from the oxide or other compound of the reactive metal. The carbide forms as a sintered mass and must be comminuted to a fine particle size for intimate mixing with finely ground oxide. Further, pellets produced from a carbide-oxide mixture are extremely dense due to the preponderance of metal content and, as a result, only moderate porosity is achieved during furnacing. To react the pellets to completion, high temperatures are necessary even during the initial and middle stages of the reaction period, during which time superficial fusion of intermediate compounds may be encountered. This results in a sealed compact from which gases are unable to escape and in a premature termination of the decarburization process.

Accordingly, it is the primary object of the present invention to provide a single-step, solid-phase process for the production of pure metal aggregates of columbium and/or tantalum.

Another object of the present invention is to provide a single-step, solid-phase process for the production of pure massive shaped metal aggregates of columbium and/or tantalum.

Other aims and advantages of the present invention will be apparent from the following description and appended claims.

In accordance with the present invention, a process is provided for the production of metal aggregates of at least one refractory metal selected from the group consisting of columbium and tantalum comprising, preparing a mixture of carbonaceous reducing agent and an oxide of the selected refractory metal. The oxide of the refractory metal is present in stoichiometric excess up to about 15 percent over stoichiometric proportions of the carbonaceous reducing agent employed for complete reduction of the metal oxide to the metal. The particle size of the oxide of the refractory metal and the carbonaceous reducing agent is within the ranges of between about 1 and 40 microns. The mixture is heated, under vacuum conditions, at a rate such that the formation of fused suboxidic compounds is averted, to a temperature between about 2000° C. and the melting point of the refractory metal being produced until substantial evolution of gas ceases to produce substantially pure solid refractory metal; and is cooled under non-contaminating conditions.

Oxides suitable for carrying out the process of the present invention are oxides of the refractory metals of columbium or tantalum. The preferred oxides for carrying out the process of the present invention are columbium pentoxide and tantalum pentoxide.

In order to produce a pure refractory metal and in the interest of facilitating the formation of a true stoichiometric mixture, a substantially pure refractory metal oxide should be employed. A standard of purity that has proved satisfactory for production of a pure metal is one wherein less than about 0.2 percent non-volatile impurities, such as vanadium, zirconium, titanium, columbium or tantalum, are present. However, in producing a pure metal, minor amounts of impurities that volatilize below the melting point of columbium and/or tantalum or that form volatile compounds may be present. For example, as much as 0.5 percent iron is tolerable in the starting materials because of the ease with which it can be driven off during the reaction. If, however, it is not important that only one pure metal be produced to the exclusion of all others, starting materials such as compounds, ores, minerals and concentrates of columbium and/or tantalum may be used, for example, columbite and tantalite. Columbite and tantallite may be conveniently described by the formula $(Fe, Mn)\cdot(Cb, Ta)_2O_6$ and are frequently columbites and tantalites of iron and manganese, with or without small amounts of one or more of such metals as titanium, zirconium, hafnium, vanadium and other refractory metals. By the process of the present invention, columbium and/or tantalum and alloys containing other elements in addition to columbium and/or tantalum may be produced.

In practicing the present invention, it has been found that the oxide of columbium and tantalum is present in stoichiometric excess over the stoichiometric proportions of carbonaceous reducing agent employed. In the pre-

ferred form of the present invention, a stoichiometric excess of between about 1 and 3 percent of the refractory metal oxide is used. It has also been found that stoichiometric excess of the refractory metal oxide can not exceed about 15 percent. Above this point, a melting effect of the suboxides occurs which serves to prevent complete decarburization.

Carbonaceous reducing agents suitable for use in the present invention are those having a percentage of fixed carbon of about 98 percent and containing as impurities substances that will, during the reaction, volatilize or form volatile compounds. For example, carbonaceous materials such as graphite, lampblack, acetylene black, thermatomic carbon and the like, are suitable for use.

Although the finely-divided starting materials, when compacted in stoichiometric proportions, maintain a desirable degree of porosity in the compact throughout the reaction, it has been found that a compact with an optimum porosity may be produced only by adding an excess of metal oxide of the metal to be produced.

It has also been found that by the addition to the charge of oxides of readily volatilized metals, such as calcium, barium, strontium and aluminum, the rate at which oxygen and carbon are removed from the charge is increased; this results in a slight increase in the porosity of the charge. However, due to the possible occurrence of explosive evolutions of gas in the furnaces, the amounts of these materials added must be carefully controlled.

In order to obtain columbium and/or tantalum with the unique physical properties possessed by the metals produced by the process of the present invention, the initial porosity of the prepared mixture is of considerable importance. Therefore, maximum surface contact must be attained between the metal and the carbonaceous reducing agent. This is accomplished by reducing the particle size of the constituents of the reaction mixture.

In practicing the present invention, the refractory metal oxide is reduced to a particle size between about 1 and 40 microns. The preferred particle size is between about 1 and 15 microns with the majority of the particles being below about 10 microns. Similarly, the carbonaceous constituent of the mixture is also reduced to a particle size between about 1 and 40 microns. The preferred particle size is between about 1 and 15 microns with the majority of the particles being below about 10 microns.

In prior art methods for the production of massive shaped metal aggregates, the starting materials were first bound with a carbonaceous binder, for example, of the Mogul type, and were subsequently either pelletized or extruded into the desired size. For example, a typical massive shaped metal aggregate was prepared with a percentage of binding material of approximately 1 to 2 percent and extruded to a nominal cylindrical size of 1½ inches in length and ¼ inch in diameter. The extruded material is then dried. After drying, it is compressed into the desired shape and subsequently furnaced for conversion into metal. If a binder is not used, the drying step can be eliminated, however, the omission of the binder frequently leads to the production of poor and unacceptable shapes.

It has now been found that in the production of pure massive shaped metal aggregates, such as consumable electrodes, bar stock and the like, the prior art multi-step operation for the production of similar massive shapes is unnecessary. In accordance with the present invention, the aforementioned constituents are prepared, intimately mixed and compacted. However, during compacting of the constituents, control of the pressure is mandatory if a pure massive shape of the mixture is to be produced. The pressure applied during compacting is confined to values up to about 1500 pounds per square inch. If pressures in excess of 1500 pounds per square inch are applied, the resulting massive shaped metal aggregate is not completely decarburized. This frequently results in production of massive shaped metal aggregates with a high-carbon content that will not meet the rigid requirements for the high-purity metal.

Table I, as set forth below, will aid in showing the criticality of the pressure during compacting in order to obtain a massive shaped metal aggregate having low carbon content and thereby avoid further processing in order to obtain an acceptable product.

Table I

Run No.	Pressure, p.s.i.	Percent Carbon in Product
1	100	0.01
2	500	0.02
3	1,000	0.03
4	1,500	0.04
5	2,000	0.23
6	40,000	0.56
7	40,000	0.46
8	40,000	0.32

The size of the massive shaped metal aggregates prepared are limited only by the equipment being used.

The reaction mixture, whether for use in the production of metal aggregates or massive shaped metal aggregates, is charged to a container of the appropriate size and shape for furnacing. Such container may be fabricated of any nonreactive material capable of withstanding temperatures of at least about 2000° C. For example, materials such as tantalum carbide or columbium carbide are suitable for use. However, it has been found that a highly suitable container is a graphite receptacle lined with a thin fused layer of either columbium oxide, tantalum oxide or sheet of columbium or tantalum metal. If columbium metal is being produced, either a columbium oxide or metal may be used as liner, so that the liner will not contaminate the metal sought and if tantalum is being produced, either a tantalum oxide or metal may be used as a liner. The liner serves the dual purpose of protecting the material from possible contamination by the container it is charged to and facilitating separation of the product from the container.

The prepared reaction mixture, charged to a suitable container, is ready for furnacing. The furnace found most suitable for practicing the process of the present invention is the induction-type furnace. However, other furnaces capable of reaching temperatures of at least about 2200° C. and amenable to operation under vacuum conditions may be employed.

The reaction mixture is placed in a suitable furnace, such as an induction-type furnace, the pressure is then decreased to about 10 microns or less. Then, under the best obtainable vacuum, the temperature of the furnace is increased to about 2000° C. or higher, but the temperature is maintained below the melting point of the metal being produced. The temperature is increased at the fastest continuous possible rate capable of attainment by the apparatus employed. For example, in an induction-type furnace, such as is used in the present invention, the preferred rate of increase of temperature ranges from about 150° C. to 300° C. per hour. During this period, the pressure within the furnace rises to about 3000 microns. If the temperature were increased at such a rate as to create a stepwise effect, superficial fusion of intermediate compounds, such as columbium monoxide and tantalum monoxide, will be encountered. This could result in incomplete reduction of the reaction mixture and, therefore, the production of a poor quality and unacceptable product. During the heating cycle, the evolved gases are eliminated from the charge and are removed from the furnace by means of a vacuum system. The reaction mixture is maintained at a temperature below the melt-

ing point of the metal being produced, but above the point where all volatile impurities will volatilize. The reaction mixture has substantially reached completion when substantial evolution of gas ceases. This can usually be determined by a noticeable decrease of the furnace pressure to approximately 0.3 micron or less. The furnace is allowed to cool to a temperature below about 600° C. at a pressure of about 0.1 micron or less. The length of time necessary to achieve this cooling is directly a function of the structural ability of the furnace itself. When cooled below about 600° C., the furnace is pressurized to about 2000 microns by the introduction of an inert gas and further cooled to a temperature below 100° C., after which the furnace is brought to atmospheric pressure and the metal removed. Any inert atmosphere that will not cause contamination of the product may be used. For example, gases such as argon and helium are suitable, while a gas such as nitrogen would not be suitable because of its contaminating effect on the product.

By adhering to the process of the present invention, the product will consist of pure columbium and tantalum. By pure columbium or tantalum is meant columbium or tantalum metal of at least about 99.8 percent purity, with the remainder being incidental amounts of impurities, such as carbon, oxygen, nitrogen, hydrogen, iron, titanium, silicon, tantalum or columbium and nickel.

The metal aggregate produced by the process of the present invention is characterized by a specific density after compacting, which density is directly affected by the particle size of the mixture. The ability to preserve a high degree of porosity during the initial and intermediate stages of the process is responsible for the preparation of a metal which, when subjected to compacting, denotes a higher density than is possible by any prior art method of preparation. The metal aggregate has an apparent density of from about 85 to 95 percent of the theoretical density of the selected metal.

A series of examples were run, for the production of pure columbium metal, according to the process of the present invention heretofore described. An induction-type furnace was used in which the reactants were charged to a suitable carbon receptacle lined with a thin sheet of columbium. The data for these tests are set forth in Table II below.

Table II

	Run 1	Run 2	Run 3
Reactants:			
Graphite (pounds)	7.7	9.5	7.9
Cb_2O_5 (99.8% pure) (pounds)	34.9	43.1	35.7
Operating Conditions:			
Reaction mixture particle size (micron)	5	5	5
Rate of heating (° C. per hour)	175	175	175
Highest temperature (° C.)	2,065	2,050	2,075
Final furnance pressure (microns)	0.4	0.6	0.6
Cooling atmosphere	(1)	(1)	(1)
Percent Yield	95.9	95.4	95.2
Product Composition, Percent:			
Columbium	99.80+	99.80+	99.80+
Carbon	0.031	0.026	0.020
Oxygen	0.02	0.03	0.04
Hydrogen	0.001	0.001	.001
Nitrogen	0.019	0.015	0.024
Remainder incidental metallic impurities			

[1] Argon.

A series of examples were run for the production of pure tantalum metal according to the process of the present invention heretofore described. An induction-type furnace was used in which the reactants were charged to a suitable carbon container lined with a thin layer of fused tantalum oxide. The data for these tests are set forth in Table III below.

Table III

	Run 1	Run 2	Run 3
Reactants:			
Graphite (pounds)	12.3	14.7	11.5
Ta_2O_5 (99.8%) (pounds)	55.7	66.5	52.0
Operating Conditions:			
Reaction mixture particle size (microns)	5	5	5
Rate of heating (° C. per hour)	200	200	200
Highest temperature (° C.)	2,065	2,050	2,075
Final furnance pressure (microns)	0.7	0.5	0.4
Cooling atmosphere	(1)	(1)	(1)
Percent Yield	94.1	99.9	98.7
Product Composition, Percent:			
Tantalum	99.86+	99.86+	99.83+
Carbon	0.039	0.032	0.032
Oxygen	0.02	0.03	0.03
Hydrogen	0.001	0.001	0.001
Nitrogen	0.009	0.009	0.007
Remainder incidental metallic impurities			

[1] Argon.

A pure massive shaped metal aggregate consisting of columbium with the remainder being incidental impurities was produced according to the process of the present invention heretofore described. An induction-type furnace was used in which the reactants were charged to a boat shaped graphite receptacle lined with high-carbon columbium metal. The data for this test are set forth in Table IV below.

Table IV

Reactants:	
Graphite (pounds)	0.53.
Cb_2O_5 (99.8% pure) (pounds)	2.42.
Operating conditions:	
Reaction mixture particle size	5 microns.
Shape (inches)	1 x 1 x 6.
Pressure to press into shape (p.s.i.)	1500.
Rate of heating (° C. per hour)	175.
Highest temperature (° C.)	2065.
Final furnace pressure (microns)	0.6.
Cooling atmosphere	Argon.
Percent yield	96.4.
Product composition, percent:	
Columbium	99.75+.
Carbon	0.05.
Oxygen	0.14.
Hydrogen	0.001.
Nitrogen	0.05.
Remainder incidental metallic impurities.	

The above examples are illustrative of the process of the present invention and are to be considered exemplary embodiments without restricting the scope of the invention.

What is claimed is:

1. A process for the production of massive shaped metal aggregates of at least one refractory metal selected from the group consisting of columbium and tantalum comprising, preparing a mixture of carbonaceous reducing agent with an oxide of said selected refractory metal, said oxide of said refractory metal being present in stoichiometric excess up to about 15 percent over stoichiometric proportions of the carbonaceous reducing agent employed, said oxide of said refractory metal and said carbonaceous reducing agent having particle sizes within the range of between about 1 and 40 microns, compacting said mixture to a massive shape at a pressure of up to about 1500 pounds per square inch; heating said mixture, under vacuum conditions, at a rate up to about 300° C. per hour to a temperature between about 2000° C. and the melting point of the metal being produced until substantial evolution of gas ceases to produce said pure massive shaped metal aggregate; and cooling said metal under non-contaminating conditions.

2. A process for the production of massive shaped metal aggregates of at least one refractory metal selected from the group consisting of columbium and tantalum compris-

ing, preparing a mixture of carbonaceous reducing agent with an oxide of said selected refractory metal, said oxide of said refractory metal being present in from about 1 to 3 percent in stoichiometric excess over stoichiometric proportions of carbonaceous reducing agent employed, said oxide of said refractory metal and said carbonaceous reducing agent having particle sizes within the range of between about 1 and 40 microns, compacting said mixture to a massive shape at a maximum pressure of 1500 pounds per square inch; heating said mixture, under vacuum conditions, at a rate up to about 300° C. per hour to a temperature between about 2000° C. and the melting point of the metal being produced until substantial evolution of gas ceases to produce said pure massive shaped metal aggregate; and cooling said metal under non-contaminating conditions.

3. A process in accordance with claim 2, wherein said carbonaceous reducing agent is graphite.

4. A process in accordance with claim 2, wherein said mixture is heated at a rate of between about 150° C. and 300° C. per hour.

5. A process for the production of massive shaped metal aggregates of at least one refractory metal selected from the group consisting of columbium and tantalum comprising, preparing a finely-divided mixture of graphite with an oxide of said refractory metal being present in from 1 to 3 percent in stoichiometric excess over stoichiometric

proportions of graphite employed, said oxide of said refractory metal and said carbonaceous reducing agent having a particle size within the ranges of between about 1 and 40 microns, compacting said mixture to a massive shape at a maximum pressure of 1500 pounds per square inch, heating said mixture, under vacuum conditions, at a rate such that the temperature of the mixture increases between about 150° C. and 300° C. per hour to a temperature of about 2000° C. and not exceeding the melting point of the metal being produced until substantial evolution of gas ceases to produce pure solid refractory metal; and cooling said metal under non-contaminating conditions.

References Cited in the file of this patent

UNITED STATES PATENTS

2,752,665	Streicher	July 3, 1956
2,785,971	Kamlet	Mar. 19, 1957
2,778,725	Brown	Jan. 22, 1957
2,839,819	Platte	June 24, 1958
2,850,378	Cooper	Sept. 2, 1958

OTHER REFERENCES

Balke: Trans. Electrochem Soc. 85 (1944), pages 89–92.

Moissan: C. R. Acad. Sci. Paris (1902), page 211.