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PROCESS FOR PRODUCING TITANIUM, ZIRCONIUM, AND ALLOYS OF TITANIUM AND ZIRCONIUM BY REDUCTION OF OXIDES OF TITANIUM OR ZIRCONIUM

Richard A. Kieffer and Friedrich Benesovsky, Reutte, Tirol, Austria, assignors to Schwarzkopf Development Corporation, a corporation of Maryland

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Because of their extremely high chemical reactivity great difficulties have been encountered in the past in producing titanium or zirconium of high purity. Many attempts have been made in the past to find a way for producing high purity titanium or zirconium by reducing their respective oxides with various reducing substances such as hydrogen, carbon, boron, silicon, aluminum, calcium, calcium hydride, calcium carbide, magnesium and the like. The heretofore proposed processes are not only very costly but they utterly fail to yield titanium or zirconium of the desired high purity. For instance, the best known processes for reducing titanium oxide with carbon within an arc body yielded a product containing only 95 to 97% titanium. Attempts to effect such titanium reduction in vacuum at temperatures up to 2400° C. have merely yielded a mixture of titanium monoxide and titanium carbide.

The present invention is based on the discovery that the difficulties encountered with prior processes are avoided and that titanium or zirconium of high purity of at least 99% may be obtained in a relatively simple way by carrying on the reduction of an oxide of either these metals with carbon or silicon or with the carbides or silicides of alloying metals of molybdenum, tungsten, chromium, nickel, aluminum, manganese, vanadium, iron and the like, in an arc maintained under vacuum at temperatures of at least 3000° C. until the reaction is completed while all oxygen and carbon containing gases produced in the reaction are being removed from the reaction space.

In accordance with the invention the titanium oxide or zirconium oxide which is to be reduced together with the reducing substance namely, carbon or silicon or the carbides or silicides of the aforenamed alloying metals are formed into arc electrodes which are used for maintaining the electric reducing arc under vacuum at temperatures of at least 3000° C. whereby the titanium or zirconium oxide of the self consuming arc electrode is reduced to titanium or zirconium of high purity. The alloying metals for producing the desired high purity alloys of titanium or zirconium may be utilized either in their metallic form or as carbides or silicides of these alloying metals or as other compounds, such as oxides of these metals.

For producing in accordance with the invention high purity alloys of titanium or zirconium, the alloying metal consisting of molybdenum, tungsten, nickel, chromium, aluminum, iron or manganese, may be used either in its metallic form or as part of a carbide, silicide or oxide of such alloying metal.

The processes of the invention are particularly suited for producing titanium or zirconium alloys of a purity of at least 99% and containing 5 to 50% of the above named alloying metals although high purity titanium or zirconium alloys of desirable properties will also be obtained with up to 95% of such alloying metal or metals.

Below are given a series of specific examples which will further illustrate the processes of the invention.

Example 1–A

For producing a high purity alloy of titanium containing 6% molybdenum, titanium monoxide in finely powdered form is mixed with molybdenum carbide in finely powdered form, the proportions of the two ingredients being so chosen that their entire carbon and oxygen content shall combine into carbon monoxide in the reaction which is carried on within the arc under vacuum at a temperature of at least 3000° C. The thorough mixture of the so proportioned two powder bodies is compacted into a rod-shaped arc electrode which is utilized to maintain a reducing arc with a cooperating arc electrode formed of a conventional water-cooled copper electrode within an evacuated vessel which is connected to a vacuum pump system so as to maintain in the interior of the vessel the desired low vacuum throughout the reducing treatment. The arc is suitably initiated between the two electrodes after first evacuating the vessel, and the reaction arc is maintained in the evacuated vessel at a temperature of at least 3000° C. such as 3010° C. while the pump system removes from the interior of the vessel the carbon oxide gas formed in the course of the reaction and there is maintained therein a vacuum of at least 10^{-5} mm. (millimeter) mercury column.

Example 1–B

A correspondingly proportioned mixture of titanium oxide, titanium carbide powder and molybdenum carbide is used for the reducing arc electrode instead of an arc electrode of titanium oxide and molybdenum carbide of Example 1–A. Otherwise the process is carried on in the same way as Example 1–A.

Example 1–C

A correspondingly proportioned powder mixture of titanium oxide, molybdenum and molybdenum carbide is used for the reducing arc electrode instead of the powder mixture of titanium oxide and molybdenum carbide of Example 1–A. Otherwise the process is carried on in the same way as Example 1–A.

Example 2–A

There is to be prepared an alloy of titanium and chromium with which there is to be formed a ternary alloy of titanium, chromium and aluminum having a high purity of at least 99%. In the initial process stage titanium dioxide powder and titanium carbide powder are mixed in such proportion that their carbon and oxygen content should be completely converted into a carbon oxide gas when subjected to the reducing reaction in an arc maintained at at least 3000° C. under vacuum. This powder mixture is then subjected to a reaction between its ingredients under a purified hydrogen atmoshpere at 2200° C., or is general at a temperature between 2000° C. and 3000° C., which yields a body containing pure titanium, titanium monoxide and titanium carbide. This mixture body is pulverized and mixed in the desired proportion with chromium powder so that the titanium and chromium content of the mixture shall correspond to the desired titanium chromium alloy. If the mixture contains oxygen in excess of the amount required for producing a carbon-oxide gas in the subsequent arc reducing reaction, some of the chromium content of the arc electrode is embodied therein as chromium carbide so that the total carbon and oxygen content of the mixture shall yield a carbon oxide gas when the powder mixture is subjected to the arc reducing reaction under vacuum at a temperature of at least 3000° C. The powder mixture so prepared is then formed into a rod shaped arc elec-

trode with which an arc reduction process, such as described in Example 1, is carried on at a temperature of 3010° C. under vacuum of at least about 10^{-5} mm.

Example 2–B

A powder mixture of titanium dioxide and fine carbon such as carbon soot is used for the powder mixture of the initial process stage of Example 2–A. Otherwise, the process is carried on as in Example 2–A.

Example 3

There is to be prepared a titanium alloy containing 2–3% aluminum and 3–5% chromium. The process is carried on in the manner explained in Example 2–A or 2–B with mixtures of titanium oxide powder, titanium carbide powder, together with aluminum powder and chromium powder, the individual powder ingredients being proportioned to yield the desired ternary alloy. The powder mixture of titanium oxide, titanium carbide, aluminum and chromium is compacted into arc electrodes which are used as self-consuming arc electrodes which maintain a reducing arc of a temperature of at least 3000° C. in an evacuated vessel as explained in the previous examples which arc reduces the titanium oxide into high purity titanium which is alloyed in the arc with the chromium and aluminum into the desired ternary alloy.

Example 4

There is to be prepared an alloy containing 20% titanium, 10% molybdenum, and 70% zirconium. Metallic molybdenum is mixed with properly proportioned powders of the oxides and/or carbides of titanium and zirconium to yield the desired ternary alloy. The amount of carbide powders in the mixture is proportioned so that its entire carbon and oxygen content shall be converted into carbon oxide gas in the arc reducing process. The powder mixture is compacted into arc electrodes which are used as self-consuming electrodes which maintain with an associated arc electrode a reducing arc at a temperature of 3005° C. in an evacuated vessel so as to yield by resulting reduction and melting process the desired ternary alloy of titanium, molybdenum and zirconium in a manner explained in the previous examples.

Throughout the specification and claims all proportions are given by weight, unless otherwise specifically stated.

It will be apparent to all those skilled in the art that the novel principles of the invention disclosed herein in connection with specific exemplifications thereof will suggest various other modifications and applications of the same. It is accordingly desired that in the present invention they shall not be limited to the specific exemplification thereof described herein.

We claim:

1. The process of reducing a metail oxide of a reactive metal selected from the group consisting of titanium and zirconium with at least one reducing substance selected from the group consisting of carbon, silicon, and the carbides and the silicides of an alloying metal selected from the group consisting of molybdenum, tungsten, nickel, chromium, aluminum, iron and manganese which process comprises mixing powder of a metal oxide of at least one of said reactive metals with powder of at least one of said reducing substances, compacting the so-mixed powders into an arc electrode, and thereafter maintaining with the so-formed arc electrode and a cooperating other arc electrode an arc under vacuum with sufficient current

to maintain the arc at a high temperature of at least 3000° C. for causing the metal oxide content of the compacted arc electrode to be reduced, and proportioning the reducing substance relatively to the reactive metal oxide of said mixed powders to produce therefrom a resultant metal body containing at most 1% by weight impurities other than the metallic content thereof, which metallic content is selected from the group consisting of titanium, zirconium, an alloy of titanium, with at least one of said alloying metals containing 5% to 95% by weight of titanium, and an alloy of zirconium with at least one of said alloying metals containing 5% to 95% by weight of zirconium.

2. The process as claimed in claim 1, said proportioning of the ingredients of said powder mixture producing a resultant metal body selected from the group consisting of titanium, zirconium, an alloy of titanium, with at least one of said alloying metals containing 50% to 95% titanium by weight, and an alloy of zirconium with at least one of said alloying metals containing 50% to 95% zirconium by weight.

3. The process as claimed in claim 1, said mixed powders being mixed to consist of at least one of said metal oxides and of a carbide of at least one of said alloying metals.

4. The process as claimed in claim 1, said mixed powders being mixed to consist of at least one of said metal oxides and of a silicide of at least one of said alloying metals.

5. The process as claimed in claim 1, wherein before maintaining the arc under vacuum with the arc electrode formed of the mixed powders, at least two different powder ingredients of the mixed powders are first treated under a protective atmosphere at an elevated temperature between 2000° C. and 3000° C. to produce a reaction between said different powder ingredients.

6. The process as claimed in claim 5, said mixed powders being mixed to consist of at least one of said metal oxides and of a carbide of at least one of said alloying metals.

7. The process as claimed in claim 1, wherein said mixed powders are mixed to consist of at least one of said metal oxides and of a silicide of at least one of said alloying metals, and wherein, before maintaining the arc under vacuum with the arc electrode formed of the mixed powders, at least two different powder ingredients of the mixed powders are first treated under a protective atmosphere at an elevated temperature between 2000° C. and 3000° C. to produce a reaction between said different ingredients.

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