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2,935,399

METHOD FOR PREPARATION OF RHENIUM

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This invention relates to the preparation of substantially pure rhenium metal for metallurgical purposes. More particularly, this invention relates to a process for the preparation of pure rhenium metal from potassium perrhenate, or ammonium perrhenate, or crude rhenium metal, wherein the pure rhenium metal product is substantially free from potassium and other impurities.

Rhenium, one of the fairly recent additions to the known elements, was discovered and isolated approximately thirty years ago. Numerous sources of rhenium have been uncovered, with rhenium in small amounts being found in the combined state in such natural ores as molybdenite and gadolinite, and with somewhat richer sources being found in some molybdenite ore concentrates and in flue-dust collections from copper ores containing molybdenite.

Numerous methods have been published and patented for the recovery of rhenium salts or metals from the natural ores and concentrates relatively rich in rhenium, and are well known to those skilled in the art. For example, U.S. Patent 2,414,965 teaches a process for rhenium recovery from flue dust and U.S. Patent 1,911,943 teaches rhenium recovery from ores containing rhenium. Usually the last step in a rhenium-recovery process involves conversion of some rhenium compound into metallic rhenium as a powder, or as some consolidated form. This powdered or consolidated form of metallic rhenium then needs to be further consolidated or compacted, as by sintering or melting, to obtain a sound, metallic structure suitable for metallurgical purposes.

In the known rhenium separation or purification methods where potassium perrhenate is an intermediate product or a starting compound, there is usually a reduction step to the crude rhenium metal and this crude rhenium metal frequently has been subjected to further process steps for removal of impurities. However, the potassium oxide, which is formed as a by-product in the potassium perrhenate reduction, is extremely difficult if not impossible to remove completely from the crude rhenium metal by leaching, washing, dialysis, or by other present-day wet chemical methods.

While rhenium is a relatively costly metal, it is finding increasing use as a special-purpose material. Many potential high-temperature applications for rhenium exist, since, among the metals, only tungsten has a higher melting point.

Rhenium metal containing impurities is difficult to fabricate. For example, potassium in excessive amounts in the rhenium apparently inhibits densification. For rhenium, it appears that a minimum sintered density or approximately 70 percent of the theoretical density of the solid metal of 21.0 grams per cubic centimeter is needed for successful cold-working of the rhenium metal.

Densification is to be understood as being a measure of the relative compactness of the metal body as compared to the theoretical density of the solid metal. The densification of a metal body with voids or porous sections, ac-

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cordingly, is less than that of a metal body having a lesser amount of voids or porous sections.

An object of this invention is to provide a method for the preparation of rhenium metal of higher purity than has previously been available from crude rhenium metal containing potassium.

Another object of this invention is a method of preparation of substantially pure rhenium metal, wherein the rhenium metal is substantially free from impurities and wherein the potassium content is low enough to permit consolidation and fabrication.

Still another object of this invention is an improved process for recovery of a pure rhenium metal wherein impurities including potassium are eliminated or reduced to a negligible amount by forming a volatile rhenium halide, selectively volatilizing the rhenium halide, subsequently hydrolyzing the rhenium halide, and converting the hydrolysis product to the pure rhenium metal.

Further objects and advantages of this invention will be readily seen and appreciated as the same become better known and understood by reference to the following detailed description when considered in conjunction with the specific examples.

The invention is a new and novel method of preparation of substantially pure rhenium metal comprising the combination of halogenation of a crude rhenium metal to a rhenium halide; selective volatilization of the rhenium halide; and conversion of the selectively volatilized rhenium halide to a substantially pure rhenium metal, by means such as hydrolysis of the rhenium halide and reduction of the hydrolysis product to a substantially pure rhenium metal that for practical purposes is free of potassium. The powder size of the pure rhenium metal is such as to lead to easy densification by methods standard to the powder metallurgy art.

In the practice of this invention, potassium perrhenate, as sold commercially, is a suitable starting material. Alternatively, potassium perrhenate, an important salt of perrhenic acid, may be prepared as a result of neutralization of perrhenic acid with potassium hydroxide or as a result of the reaction of potassium chloride with perrhenic acid. Perrhenic acid may be prepared in several ways. One of the most common is the combination or solution of rhenium heptoxide with water. Numerous other methods for the preparation of potassium perrhenate are known to those skilled in the art.

Alternatively, ammonium perrhenate may be used as the starting material. The ammonium perrhenate may be prepared by the neutralization of perrhenic acid with ammonium hydroxide; or the ammonium perrhenate may be prepared from potassium perrhenate by a reduction to the rhenium metal with subsequent oxidation of the rhenium metal to a rhenium oxide which is treated with ammonium hydroxide; or ammonium perrhenate may be prepared by other means well known to those skilled in the art.

Alternatively, scrap rhenium metal or crude rhenium metal which, as such, is not capable of fabrication may be used as the starting material or may be used in combination with crude rhenium metal obtained from numerous starting materials.

Any, or all, or combinations of any or all, of the rhenium materials mentioned may be used as suitable alternative starting materials where it is desired to reduce potassium and other impurities in the rhenium metal product to a negligible amount.

In the practice of this invention wherein potassium perrhenate is the starting material, the first step of the process is the reduction of the potassium perrhenate to a crude rhenium metal. The second process step is the halogenation of the crude rhenium metal to a volatile rhenium halide. The third process step is the selective

volatilization of the rhenium halide. The fourth process step is the subsequent hydrolysis of the volatile rhenium halide, and the fifth process step is the reduction of the products of hydrolysis to rhenium metal containing only a negligible amount of potassium and other impurities.

In the practice of this invention wherein ammonium perrhenate is the starting material, the first step is the heating of ammonium perrhenate in a hydrogen atmosphere to obtain a crude rhenium metal. The second step and subsequent remaining steps of the process are the same as in the practice of the invention wherein potassium perrhenate is the starting material.

In the practice of this invention wherein scrap rhenium metal or crude rhenium metal having a potassium content, which, as such, is not capable of fabrication, or wherein crude rhenium metal in combination with scrap metal, or with metal incapable of fabrication, are the starting materials, the initial step is the halogenation of the rhenium metal to a volatile rhenium halide. The next process step and the remaining process steps are the same as the third process step and the subsequent remaining process steps, as in the practice of the invention wherein either potassium perrhenate or ammonium perrhenate is the starting material.

In the following examples, Examples I and II are illustrative of conventional practice, while Examples III and IV are illustrative of the present invention. The examples of the present invention are to be construed as merely illustrative and not as limiting the scope of the present invention.

Example I

Rhenium powder was prepared by the hydrogen reduction of commercial potassium perrhenate in the following manner: approximately 1000 grams of potassium perrhenate were reduced in a heated stainless steel vessel by the addition of hydrogen gas. Prior to the addition of hydrogen gas, the vessel and contents were preheated to 250° C. and this temperature was maintained for the first hour of reduction. At this time the vessel and contents were heated to 500° C. and maintained at 500° C. for approximately three hours. The reduction may be considered completed when condensation of moisture can no longer be detected from the exiting gas. Then, the vessel and contents were permitted to cool to approximately room temperature and the hydrogen gas flow stopped. The contents were removed from the vessel. The product was leached with distilled water to remove substantial amounts of potassium hydroxide. The product was then returned to the reduction vessel and reduced further by hydrogen gas with the vessel and contents at 1000° C. for two additional hours to obtain the crude rhenium metal powder. The crude rhenium metal was leached with distilled water, then leached with a dilute aqueous acid solution of 10 percent hydrochloric acid by volume, and then leached with additional distilled water in an effort to remove potassium from the crude rhenium metal.

Approximately 93 percent of the rhenium was recovered as crude rhenium metal powder. A chemical analysis was made of the crude rhenium metal powder obtained with the potassium content analyzing .50 percent.

Example II

The ammonium perrhenate for this example was prepared from potassium perrhenate by a hydrogen reduction to the rhenium metal with subsequent oxidation of the rhenium metal to a rhenium oxide which was treated with ammonium hydroxide to obtain the ammonium perrhenate. Approximately 350 grams of rhenium powder were prepared from ammonium perrhenate in the following manner: 500 grams of finely divided ammonium perrhenate, having a potassium content of .47 percent, were heated gradually to 1000° C. in a closed "Vycor" vessel with pure, dry hydrogen gas passing for approximately two hours through an entrance tube into the ves-

sel, circulating through the ammonium perrhenate, and exiting through an exit tube attached to the vessel. "Vycor" is the name of a low-expansion glass consisting essentially of silica that is marketed and sold by the Corning Glass Company, Corning, New York. The ammonium perrhenate decomposed to give ammonium hydroxide, water, and a black powder. As the heating continued, the black powder was reduced by the hydrogen atmosphere to a crude rhenium metal powder. The heat was discontinued and the hydrogen gas flow continued until the vessel and product, rhenium metal, reached room temperature.

A chemical analysis was made of the crude rhenium metal powder obtained with the potassium content analyzing .40 percent.

Example III

The crude rhenium metal for this example was a composite mixture of crude rhenium metals prepared by the processes as illustrated in Examples I and II. Approximately 300 grams of crude rhenium metal powder, having a potassium content of .40 percent, were exposed to hydrogen gas at 800° C. for two hours by passing the hydrogen gas through the rhenium metal powder in a "Vycor" apparatus to convert any rhenium metal oxides present to crude rhenium metal. The rhenium metal powder was cooled to 700° C. with a purging flow of helium gas flowing through the apparatus.

The helium gas inlet was closed and commercially available tank chlorine gas admitted at a rate sufficient to maintain a small positive pressure within the apparatus as shown by the flow from the exit line of the apparatus. The rhenium metal powder was converted to rhenium pentachloride, which condensed in or near the exit flow line. The rhenium metal chlorinated at a rate of approximately 150 grams per hour with all the rhenium apparently converted to the pentachloride. The condensed rhenium pentachloride was flamed with a hand torch at intervals, driving the pentachloride into a collecting vessel which was maintained at approximately room temperature.

The rhenium pentachloride was hydrolyzed by adding it slowly and cautiously to distilled water cooled to about 10° C. by an ice bath. The reaction was accompanied by vigorous boiling and the formation of an extremely fine particle-size precipitate. (If the hydrolysis is not carried out in cool water the yield is somewhat lower.) The precipitate was filtered from the filtrate onto medium retention filter paper. The precipitate was air-dried, and then dried further in a desiccator using calcium sulfate hemihydrate as a desiccant.

A few grams of the dried precipitate were reduced by hydrogen gas at 600° C. in one hour to obtain the purified rhenium metal. Later some additional precipitate was reduced at 600° C. to obtain approximately 200 grams additional pure rhenium metal.

A chemical analysis was made on the purified rhenium metal and the total impurities found analyzed .05 percent. The analysis showed a 0.00 percent potassium content. The analysis for potassium had a sensitivity sufficient to detect potassium contents as low as .001 percent.

Example IV

An approximately 300-gram mixture of approximately 50 percent crude rhenium metal and 50 percent scrap rhenium metal was converted to substantially pure rhenium metal by the process of this invention. The exact impurity content of the crude rhenium metal was not known. The crude rhenium metal had been obtained by the process illustrated in Examples I and II, where in all previous runs crude rhenium metal containing in excess of .20 percent impurities was obtained. The exact impurity content of the scrap rhenium metal was not known. However, the scrap rhenium metal was metal incapable of fabrication because of insufficient densifi-

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cation, and its behavior under fabrication attempts resembled that of rhenium metal containing sufficient potassium to inhibit densification.

The rhenium metal mixture was placed in a vessel of "Vycor" and the vessel and contents heated to 750° C. with a purge of helium flowing through the mixture and vessel. The helium flow was stopped and at the same instant a flow of commercially available tank chlorine gas was supplied to the vessel and contents. The chlorine gas flow was continued for two hours \pm 15 minutes with the vessel and contents at 750° C. The rhenium metal chlorinated at a rate of approximately 150 grams per hour. The volatile rhenium pentachloride was collected in an attached collecting vessel.

The rhenium pentachloride was slowly and cautiously reacted with distilled water to obtain a fine particle-size precipitate. Three filtrations were made of the filtrate to collect the precipitate. The precipitate was air-dried and then dried further in a dessicator using calcium sulfate hemihydrate as a dessicant.

The dried precipitate was reduced by hydrogen gas at 600° C. to obtain pure rhenium metal with approximately 87 percent of the theoretical yield of pure rhenium being obtained.

Example I illustrates a conventional preparation of crude rhenium metal from potassium perrhenate. The crude rhenium metal after several leachings, including one with a dilute aqueous acid solution, still contained a substantial potassium content.

Example II illustrates that a conventional method of preparation of crude rhenium metal from ammonium perrhenate with a substantial potassium content gives a rhenium metal having a substantial potassium content.

Examples III and IV illustrate the method of this invention wherein crude rhenium metals with a substantial potassium or impurity content are converted into pure rhenium metal. The potassium or total impurities in the product metal are negligible for metallurgical purposes.

In the step of preparing the crude rhenium metal from potassium perrhenate by hydrogen reduction a maximum temperature of 500° C. is preferred. At a temperature of approximately 550° C., melting of the potassium perrhenate is likely to occur. While the hydrogen reduction of potassium perrhenate has been accomplished successfully at temperatures slightly above 500° C., difficulty has been encountered when attempting to use a 550° C. temperature.

In the step of halogenation of the crude rhenium metal, where the halogenation is a chlorination, temperatures ranging from 600° C. to 800° C. have been used. A temperature of 750° C. is the preferred chlorination temperature. The rate of chlorination appears to be dependent on the chlorination temperature with little increase in rate of chlorination at temperatures greater than 750° C., and with rapid decreases in the rate of chlorination at temperatures lower than approximately 600° C.

In the separation of the precipitated product of the hydrolysis step, filtration time may be reduced substantially by bubbling carbon dioxide gas through the water containing the product for about 30 minutes before filtering. Rhenium remaining in the filtrate may be recovered by treating the filtrate with a small amount of 30 percent hydrogen peroxide solution to obtain a perrhenic acid solution which may be neutralized by ammonium hydroxide to obtain ammonium perrhenate which may be converted to crude rhenium metal for subsequent recycling in the process of this invention.

In the step of hydrogen reduction of the product obtained from the hydrolysis of the volatilized rhenium halide, it is preferred that the temperature be raised stepwise to a maximum temperature of approximately 600° C. and that the maximum reduction temperature be maintained for a sufficient period of time to accomplish the reduction. Successful reductions of the hydrolysis product have been made at maximum temperatures as

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high as 1000° C. The particle size of the rhenium metal obtained from the hydrogen reduction of the hydrolysis product appears to be dependent on the reduction temperature with the finer particle size obtained at the lower temperatures.

Numerous unsuccessful attempts were made to metallurgically process crude rhenium metal as obtained from the hydrogen reduction of potassium perrhenate, as illustrated in Example I, and from the decomposition-reduction of ammonium perrhenate, as illustrated in Example II. In a few instances proper pressing of the crude rhenium powder was achieved, but in no instance, after sintering, was a densification of the powder body obtained sufficient to permit metallurgical processing and fabrication, where the potassium content of these rhenium metals exceeded .05 percent. The crude rhenium metals in these unsuccessful metallurgical processing attempts generally had potassium contents ranging from 0.06 percent to 0.60 percent. Varied particle-size crude rhenium powders were utilized with insufficient improvement in densification to permit metallurgical processing.

However, rhenium metals prepared by the method of this invention, as illustrated in Examples III and IV, with only a very small or negligible potassium content, were successfully pressed, sintered, and metallurgically processed. Almost invariably, densifications from sintering in excess of 70 percent of theoretical density were obtained and the sintered rhenium powder body was successfully metallurgically processed.

The preparation of a sintered metal rhenium body by pressing and sintering was in accordance with known methods of the powder metallurgical art. The sintered and densified rhenium metal body was metallurgically processed by suitably selected cold working of the body prior to heavier cold reductions. In the heavier cold reductions, annealing of the metal body was necessary and the amount of reduction was controlled and limited in a stepwise procedure in that a reduction of the rhenium metal body was made, then the body was annealed. This was then followed by subsequent reductions plus annealings to eventually obtain the desired dimensions.

Pure rhenium metal prepared by the process of this invention, as illustrated in Example III and IV was successfully metallurgically processed and physical properties of the pure rhenium metal measured. Pure rhenium metal prepared, as illustrated in Example III, was pressed and sintered to obtain a densification of approximately 80 percent of theoretical density. Annealed rhenium rods (0.05 inch in diameter) from the metallurgically processed rhenium metal, prepared as illustrated in Example III, gave a tensile strength of 171,000 p.s.i., an elongation of 15 percent, and, in the annealed state, a Vickers hardness of less than 300 V.H.N.

The physical properties of the pure rhenium metal, prepared by the process of this invention, after metallurgical processing are at least the equivalent and generally are superior to the physical properties of rhenium obtained by any other known process. For example, Agte and his coworkers in "Physical and Chemical Properties of Rhenium," *Z. anorg. m. allgem. Chem.*, 119, 129-159 (1931), report a tensile strength for rhenium of 70,000 p.s.i. for rhenium specimens prepared by a hot-wire deposition process.

The scope of possible applications for rhenium metal has been greatly enhanced by this invention wherein rhenium metal with improved physical properties may be obtained. While the exact reason for the improved physical properties of the rhenium of this invention is unknown, it is believed and theorized that the minimization of potassium and other impurities in the rhenium has permitted the obtaining of the improved properties.

While the specific procedures and examples given have been only of the chlorination of the crude rhenium metal as the preferred treatment, it is to be understood that this invention is not so limited and, that, as will be obvious

to others skilled in the art, a member selected from the group consisting of fluorine, chlorine, and bromine of group VII of the periodic table may be used in the halogenation step. These members of group VII of the periodic table are commonly known as halogens and the generic reaction of a member of the group with rhenium to give a rhenium halide is known as halogenation.

It is to be understood that rhenium halide as used in the specification and claims is inclusive of all volatile halides or volatile complex halides of rhenium and fluorine, chlorine, and/or bromine. It is to be understood that the term rhenium chloride as used in the specification and the claims is intended to include all volatile rhenium chlorides. Rhenium-chlorine binary compounds corresponding to several oxidation states are known. In a like manner, rhenium fluoride includes all volatile rhenium fluorides and volatile complex fluorides and rhenium bromide includes all volatile rhenium bromides or volatile complex bromides.

While the specific procedures and examples given have illustrated the conversion of the selectively volatilized rhenium halide to a substantially pure rhenium metal by the preferred method of hydrolysis of the selectively volatilized rhenium halide and reduction of the hydrolysis product to a substantially pure rhenium metal, it is to be understood that this invention is not so limited. Other means known to those skilled in the art may be used. For example, the selectively volatilized rhenium halide may be converted to a substantially pure rhenium metal by hydrogen reduction, or by conversion to an oxide followed by subsequent reduction, or by other means well known to those skilled in the art.

This invention permits the preparation of a pure rhenium metal of adequate purity for metallurgical purposes. The potassium and other impurities in the purified rhenium metal are held to a negligible quantity, thus facilitating the consolidation of the purified metallic rhenium to a sound, metallic structure for metallurgical purposes and permitting the obtaining of improved physical properties in the sound, metallic structure.

While a preferred method has been shown and described, it will be obvious to those skilled in the art that various changes and modifications may be made without departing from the invention in its broadest aspects and the appended claims are intended to cover all such changes and modifications as follow within the true spirit and scope of the invention.

What is claimed is:

1. A method for obtaining a substantially free-from-potassium, purified rhenium metal powder for metallurgical consolidation and fabrication from a crude rhenium metal containing potassium, the method comprising: preparing a volatilization product by exposing the crude rhenium metal containing potassium to a halogen selected from the group consisting of fluorine, chlorine, and bromine at an elevated temperature sufficient to form and to volatilize a rhenium halide transferring the volatilization product in a gaseous state to a situs other than the situs of the preparation of the volatilization product; condensing the transferred volatilization product; contacting the condensed volatilization product with water to form a rhenium hydrolysis product; and reducing the rhenium hydrolysis product with hydrogen to provide the substantially free-from-potassium, purified rhenium metal powder.

2. The method of claim 1 in which the halogen is fluorine.

3. The method of claim 1 in which the halogen is chlorine.

4. The method of claim 1 in which the halogen is bromine.

5. The method of claim 1 in which the halogen is chlorine and in which the method includes the preparation of the crude rhenium metal containing potassium by a hydrogen reduction of potassium perrhenate.

6. The method of claim 1 in which the halogen is chlorine and in which the method includes the preparation of the crude rhenium metal containing potassium by a hydrogen reduction of ammonium perrhenate containing potassium.

7. A method for obtaining a substantially free-from-potassium, purified rhenium metal powder for metallurgical consolidation and fabrication from a crude rhenium metal containing potassium, the method comprising: exposing the crude rhenium metal containing potassium to a halogen selected from the group consisting of fluorine, chlorine, and bromine at an elevated temperature sufficient to form and to volatilize a rhenium halide to form a volatilization product; transferring the volatilization product in a gaseous state to a situs other than the situs of the formation of the rhenium halide; contacting the transferred volatilization product with water to form a rhenium hydrolysis product; and reducing the rhenium hydrolysis product with hydrogen to provide the substantially free-from-potassium, purified rhenium metal powder.

8. The method of claim 7 in which the halogen is chlorine and the rhenium halide is a rhenium chloride.

9. The method of claim 8 in which the rhenium chloride is rhenium pentachloride and in which the method includes the preparation of the crude rhenium metal containing potassium by reducing potassium perrhenate with hydrogen.

10. The method of claim 8 in which the rhenium chloride is rhenium pentachloride and in which the method includes the preparation of the crude rhenium metal containing potassium by reducing an ammonium perrhenate containing potassium with hydrogen.

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