Nov. 29, 1966 H. R. SMITH, JR., ETAL 3,288,593

PURIFICATION OF METALS

Filed Nov. 8, 1963 3 Sheets-Sheet 1

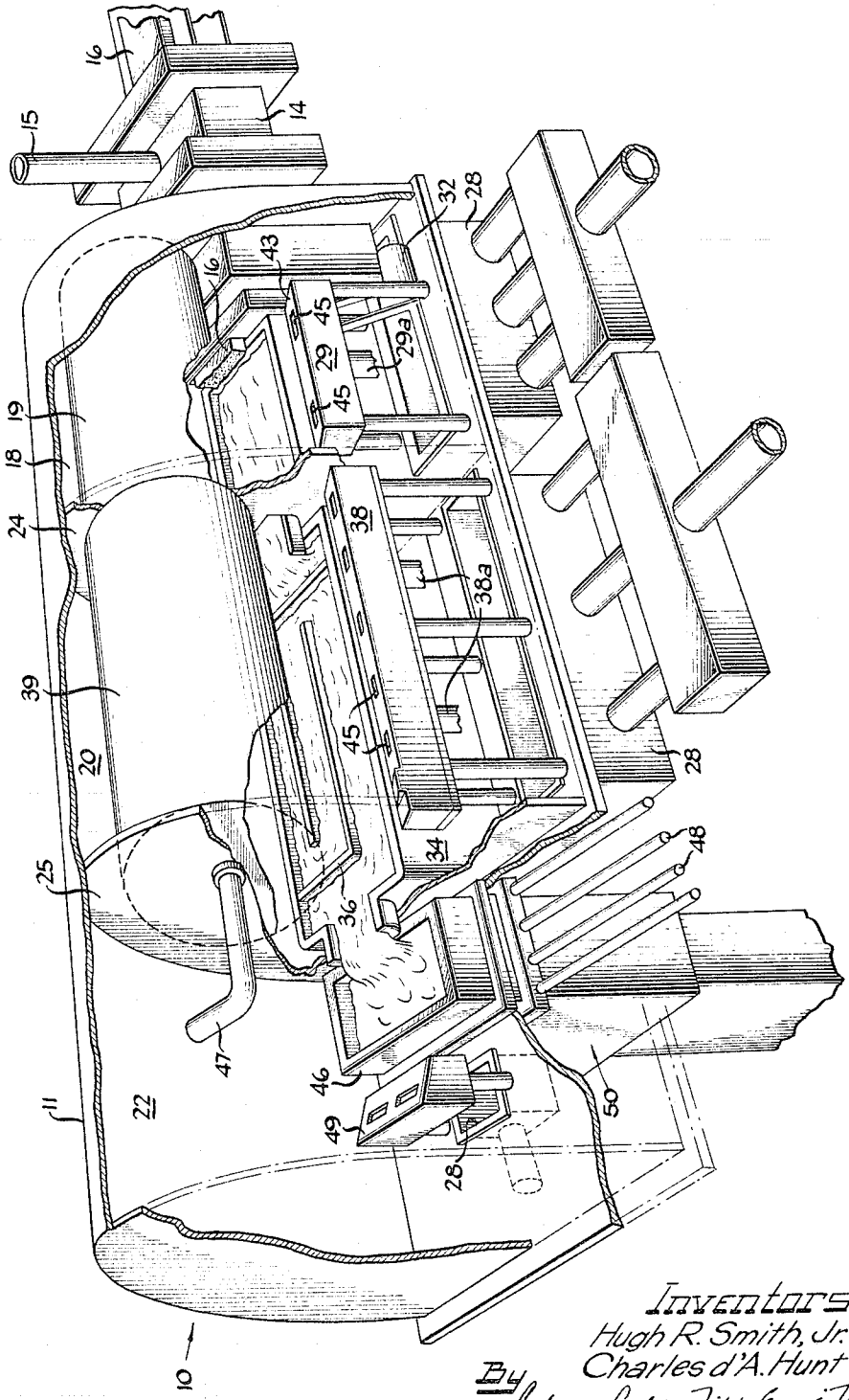


Fig 1

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PURIFICATION OF METALS

Filed Nov. 8, 1963 3 Sheets-Sheet 2

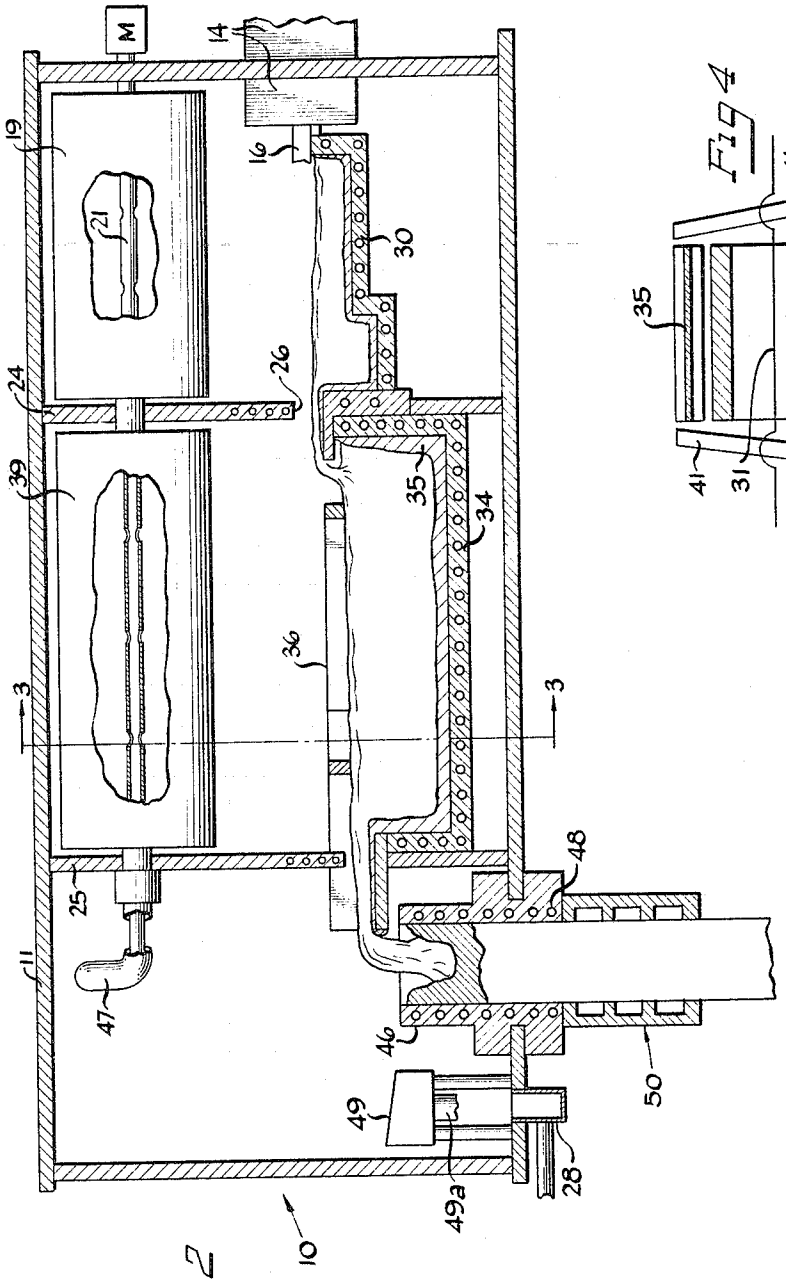


Fig 2

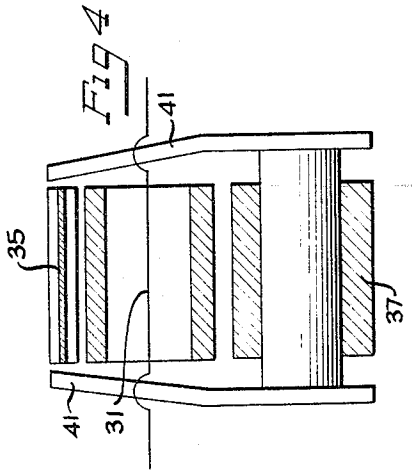


Fig 4

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PURIFICATION OF METALS

Filed Nov. 8, 1963 3 Sheets-Sheet 3

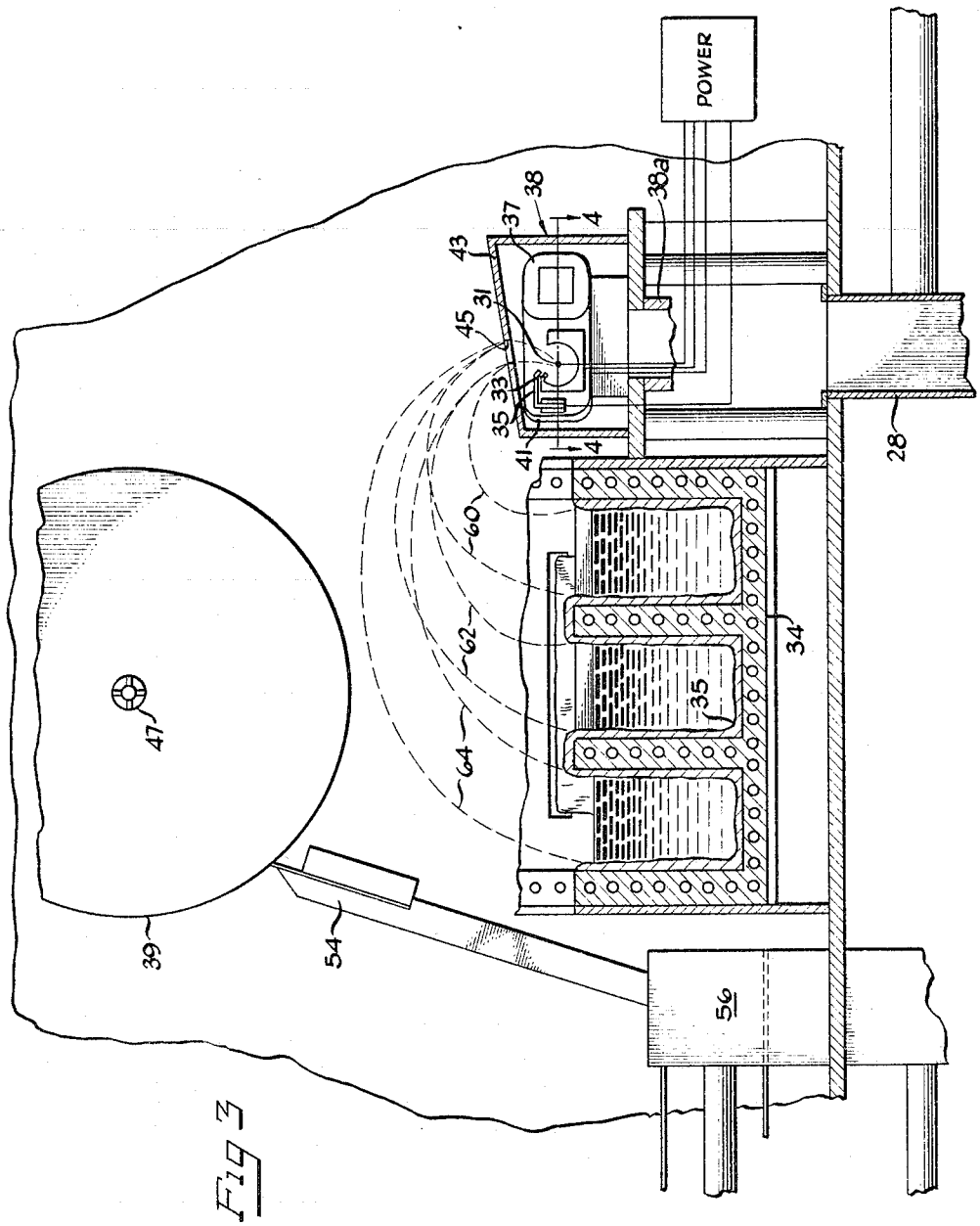


Fig 3

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PURIFICATION OF METALS

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16 Claims. (Cl. 75—84)

This invention relates to the production of relatively pure metals and metal alloys, and more particularly to an economical method and apparatus for the production of such relatively pure metals and metal alloys.

The purification of metals and alloys has long presented a problem to metallurgists; and, although processes for producing most metals and alloys have been generally set forth, these processes frequently involve apparatus and process conditions that prevent the production of particular metals and alloys at reasonable costs. Thus, the price of some metals and alloys has been so high that their use has been limited.

Technological and scientific advances of recent years have developed new uses for some of the heretofore expensive metals, if they could be produced at lower costs. In general, the new uses for these metals and alloys also require a higher degree of purity than has heretofore been possible.

Conventional processes for refining metals include electrolysis and distillation, among other techniques. Although electrolysis can be used to produce metals of fairly high purity, contamination of the metal by constituents of the electrolyte, as well as by the materials of construction of the electrolytic cell, causes severe problems. In addition, electrolytic processes involve very high capital costs per unit of product output.

Distillation processes have also been used, but invariably involve very high operating costs because of the difficulty of supplying the required quantity of heat to the crude stock at a rate which is sufficient to cause a rapid distillation of the stock. Distillation processes are also generally disadvantageous due to the materials of construction problems associated with high temperature operations involving metals and metal compounds. Contamination of the distillate because of interaction between the melt and the container material also presents difficulty in conventional high temperature distillation operations. Generally, whenever the problem of producing a highly purified metal or alloy has been solved satisfactorily, the economics of producing the metal or alloy have been such as to seriously limit the use of these ultra pure products.

It is a principal object of the present invention to provide an economical method for the production of metals and metal alloys of high purity from low cost raw materials. It is another object of this invention to provide an economical method and apparatus for the production and purification of metals to a degree of purity which has been heretofore unobtainable except at high cost. A still further object of this invention is to provide a method for the production of pure metals and alloys which employs the use of naturally occurring ores and other available metallic compounds as starting materials. An additional object is to provide a continuous process for the production of pure metals and alloys. Yet another object of the present invention is to provide an apparatus for the production of pure metals and alloys which has a long life.

These and other objects of the invention are more particularly set forth in the following detailed description and accompanying drawings of which:

FIGURE 1 is a partial perspective schematic view of one form of apparatus for carrying out a preferred embodiment of the method of the invention;

FIGURE 2 is a vertical cross section of the apparatus of FIGURE 1;

FIGURE 3 is an enlarged fragmentary cross sectional view taken generally along line 3—3 of FIGURE 2; and

FIGURE 4 is an enlarged horizontal cross sectional view taken generally along line 4—4 of FIGURE 3.

In general, the method of the present invention comprises the vaporization of impurities from a metal or metal alloy to be produced in pure form under conditions which provide very high rates of vaporization and long apparatus life. More specifically, the method in accordance with the present invention comprises the reduction of a compound of a metal to be purified with a reducing agent, and the vaporization of excess reducing agent present, if any, the reducing agent compounds formed and other volatile impurities from the product metal at a reduced pressure and at a temperature which is sufficient to vaporize the volatile impurities, excess reducing agent and reducing agent compounds at the reduced pressure, but which is insufficient to vaporize the product metal to any appreciable extent.

At the operating temperature and pressure the reducing agent reduces the metal compound raw material, and a mixture of the reducing agent, reducing agent compounds and the metal to be purified is formed. The reducing agent also reacts with substantially all of the non-volatile impurities associated with the raw materials. The reducing agent is preferably selected so that both the reducing agent and the reducing agent compounds formed during the reduction process are more volatile at the operating pressure and temperature than the metal product. The metal product, from which substantially all of the impurities have been vaporized, is recovered by solidfication in a purified condition which has heretofore been unobtainable. The vaporized excess reducing agent, reducing agent compounds and volatile impurities are recovered from the apparatus by condensation upon a condenser surface or are removed as gases from the purification apparatus.

Preferably, the process is carried out utilizing an apparatus having at least two pressure regions, a preheat region maintained at a reduced pressure within the range of about 500 microns of mercury to about 1 to 2 microns of mercury, and a purification region maintained at a reduced pressure within the range of not more than about 1 to 2 microns of mercury and preferably less than 0.1 micron of mercury. At pressures within the indicated range and at the operating temperatures, the volatility of the product metal is substantially less than the volatility of the reducing agent, the reducing agent compounds formed and the volatile impurities. The differing volatilities at the low operating pressure and high temperature causes the vaporization of the excess reducing agent, reducing agent compounds and volatile impurities without any appreciable vaporization of the product metal.

The process, as outlined, has been found to be particularly suitable for the purification of metals such as columbium, tantalum, molybdenum, tungsten, hafnium, zirconium and rhenium, these metals generally being considered difficult to economically produce in ultra-pure form. In conjunction with this, the oxides of these metals, which occur naturally in the form of ores or which are easily formed by conventional oxidizing processes have been found to be a convenient form of raw materials, as the oxides are easily reacted with reducing agents utilizing the distillation techniques set forth hereinbelow. The raw materials, which can be a relatively pure oxide or an ore concentrate having as little as 50 percent of the desired metal oxide may be compacted into suitable shapes for ease in handling prior to intro-

duction into the purification apparatus, or can be placed in metal boxes or containers which become melted and subsequently distilled during the process. In conjunction with this, boxes formed of sheet iron have been found to be desirable.

The only limitation placed on the reducing agents that can be employed within the scope of the present invention is the relative volatilities of the reducing agent and reducing agent compounds formed during the reduction reaction compared to the volatility of the metal to be purified. At the purification pressure and temperature the volatility of the reducing agent compounds should be greater than the volatility of the metal to be purified. Preferably, the reducing agent is selected so that the reducing agent compounds formed are also more volatile than the reducing agent. By employing reducing agents of this nature all of the associated impurity with the product metal will react with the reducing agent and will be vaporized before any appreciable amount of the reducing agent will be vaporized, allowing the use of approximately stoichiometric amounts of the reducing agent.

Economically, silicon which has a relatively highly volatile monoxide, is a preferred reducing agent, but aluminum and other metals having a relatively highly volatile monoxide, including the rare earth metals such as cerium and lanthanum are also operable. The reducing agent need not be in a highly purified form. For instance, commercial silicon containing as much as 0.05 percent carbon may be used in the purification of metal oxide ores. When the reducing agent contains carbon impurities or other impurities that form vaporizable compounds with the cation of the product metal compound raw material at the operating conditions, an amount of reducing agent correspondingly less than the stoichiometric amount is employed so that the carbon or other impurity combines with the product metal cation, e.g., the oxygen of the product metal oxide raw material, at the operating temperature and pressure and is vaporized from the product metal, e.g., as carbon monoxide vapor. If the raw materials contain a stoichiometric amount of reducing agent so that all of the impurities associated with the raw materials preferentially react with the reducing agent, the carbon or other nonvolatile impurity in the reducing agent may not be completely vaporized and will contaminate the product, necessitating a subsequent purification step to obtain a product of the desired purity.

The method of the present invention may also be employed as a final purification stage for a crude intermediate metal product obtained from a conventional reduction process. In such instances the raw material ore is partially purified according to known procedures, generally at or near atmospheric pressure. The crude intermediate product from the known purification process is then purified according to the method herein described to provide a highly purified product. This procedure is particularly suited for use with ores which, for one reason or another, cannot be used as raw materials in the hereinafter described apparatus.

Although the process may be carried out in an apparatus having a single purification region, as set forth above, the process is preferably carried out in an apparatus having two or more regions. An example of a particular apparatus is one which includes a preheat region, a purification region, and a product withdrawal region, which regions are desirably maintained at different temperatures and pressures. The preheat region of the apparatus is preferably maintained at a temperature and reduced pressure so that a substantial portion of the more volatile impurities and reducing agent compounds formed may be economically vaporized and removed from the raw materials. The temperature and pressure within the preheat region is preferably selected so that the raw material feedstock is melted and the volatile materials are vaporized without causing excessive splatter of the substantially molten raw materials due to violent evolution of the volatile materials from the molten raw materials. At the same time, the temperature and pressure within the preheat region is preferably selected so there is minimal vaporization of the desired metal product.

The temperature and reduced pressure within the purification region is selected so that a molten pool of reactants will be maintained throughout the reduction and purification process. If the reactants mixture in the purification region becomes solidified at the operating pressure and temperature, excessive amounts of the desired metal product may be vaporized due to localized superheating at the surface of the solid mixture. It has been found however, that if the mixture is maintained in a molten state throughout the purification process, the tendency of the metal product to be vaporized is greatly diminished and a highly purified product can be obtained without substantial loss thereof due to vaporization.

The only operable apparatus for carrying out the described process to the high degree of purity contemplated is an electron beam furnace, one form of which is shown in the attached drawings. An electron beam furnace can be made to operate at pressures approaching one-tenth of one micron of mercury or less and has the desirable characteristics of a complete absence of a reactive atmosphere and the absence of the introduction of any impurities into the metal to be purified by the electron beam during the purification process.

Now referring to the drawings in detail, there is shown in FIGURE 1 a preferred form of an electron beam furnace **10**. The furnace **10** has a vacuum tight elongated housing **11**, and has a vacuum lock inlet **14**, connected by a pipe **15** to suitable vacuum pumps, not shown, through which the raw materials **16** enter the furnace. The furnace **10** is advantageously divided into three regions, a preheat region **18**, a purification region **20**, and a product withdrawal region **22**, which regions are formed by a pair of spaced apart walls **24** and **25** disposed intermediate to the end walls of the housing **11**.

Each of the regions of the furnace **10** may be maintained under a high vacuum by one or more conventional diffusion pumps connected to manifolds **28** located in the bottom wall of housing **11**. In some instances where an extreme vacuum is not required a Roots blower type of mechanical pump may be used in place of a vacuum diffusion pump. The vacuum diffusion pumps handle only the volatile noncondensible impurities evolved during the purification process, such as carbon monoxide, oxygen and nitrogen, the large bulk of the vapors generated during the process being condensed on the hereinafter described condenser substrates without substantially affecting the overall pressure within the housing **11**. The diffusion pumps can be adjusted to maintain the same or different degrees of vacuum within the regions **18**, **20** and **22**, respectively, as may be desired. Generally a higher vacuum, i.e., a lower pressure, is desired within the purification region **20** than is necessary in the preheat region **18** or the product withdrawal region **22** since the final portions of the reducing agent and reducing agent compounds are vaporized from the metal product in this region. The final separation of the reducing agent and reducing agent compounds from the product metal is enhanced by a higher vacuum, the higher vacuum giving a greater degree of separation.

The raw materials **16** are introduced in the preheat region **18** through the vacuum lock **14** by a suitable mechanical pusher or ram (not shown) and are directed into a water cooled support structure **30**, which may be constructed from any suitable material such as copper. The preheat region is desirably maintained at a reduced pressure within the range of about 1 to 500 microns of mercury, preferably, about 10 to 200 microns of mercury.

Disposed adjacent the support structure **30** is an electron beam gun housing **29** in which are housed a plurality

of electron beam guns. In order to economically produce metals and metal alloys by the above outlined process, the process preferably proceeds via a rapid vaporization of the volatile impurities and impurity containing compounds from the product metal containing raw material feedstock. The rapid vaporization of the impurities and impurity containing compounds results in the formation of a high local pressure of distillate vapor surrounding the surface of the vaporizing feedstock. Electron beam heating provides the means for supplying heat at the required rates for rapid vaporization on a highly economic basis. The electron beam energy is particularly efficient since it is transferred directly to the interface of the feedstock where the phase change from solid to vapor, or liquid to vapor is occurring. In order to operate at maximum efficiency, the electron beam generating apparatus must be maintained within a region of lower pressure, e.g., high vacuum, which is provided by vacuum diffusion pumps and as shown in FIGURE 1, the electron beam gun housing **29** is preferably directly connected to the diffusion pumps by a pipe **29***a* to provide a maximum vacuum adjacent the electron guns.

One form of available electron gun which is particularly suitable for use in the electron beam furnace is illustrated by FIGURES 3 and 4. The electron gun comprises an elongated emissive filamentary cathode **31**, a cathode focusing structure **33** and an anode **35**. The cathode **31** may be in the form of an elongated rod or other suitable shape and is designed to project an elongated and narrow electron beam. The beam is focused and directed by an electron focusing magnet, including a coil **37** and pole pieces **41**, which straddles each of the electron guns as generally shown in FIGURE 4. The magnetic pole pieces **41** are arranged to provide a barrel shaped field for a purpose hereinafter described. The housing **29** which is formed from a nonmagnetic material shields the electron guns from ions liberated during the purification process. The upper wall **43** of the housing **29** contains narrow slits **45** through which the electron beam is caused to pass by the focusing magnet pole pieces **41**. The cathode **31** is heated to an electron emissive temperature by the passage of current therethrough and the emitted electrons are attracted by the anode **35** which is maintained at a positive potential with respect to the cathode. The attracted electrons are focused into a beam by the magnetic field established in the gap between the pole pieces **41**. Each of the beams, indicated generally by **60**, **62** and **64**, is curved and is compressed into a circle by the barrel shaped magnetic field established between the pole pieces **41**. The shape of the different electron beams may be adjusted in a known manner by adjusting the field of the various magnets.

It has been found that optimum results are obtained when the preheat region of the furnace is maintained at an operating pressure and temperature so that the purification is completed in the preheat region **18** to the extent that the raw material feedstock is melted to form a molten pool of reactants and as much of the volatile impurities, e.g., sulfur, and the more volatile reducing agent compounds that are formed are vaporized as is economically convenient.

The particular operating temperature and pressure are desirably chosen so as to cause vaporization of a major portion of the volatile materials, at a relatively higher absolute pressure, e.g., 1 to 500 microns of Hg, in the preheat region **18**. The removal of a maximum or optimum amount of the volatile materials, both condensible and noncondensible, at a relatively higher pressure in the preheat region **18** lessens the overall volumetric pumping requirements of the vacuum pumps for a given mass flow, both in the preheat region **18** and in the purification region **20**. Of course, the particular operating conditions for the preheat region **18** will vary for different raw materials and for differing degrees of purity required in the product. However, efficient control of the operating temperature and pressure, and the pumping requirements of the vacuum pumps, in preheat region **13** may be effected to cause the evolution of an optimum amount of the volatile materials from the molten reactants, thereby enhancing the overall economics of the process. Generally, about one-half to two-thirds or more of the volatile materials may be vaporized in the preheat region of the electron beam furnace.

The reducing agent compounds vaporized are condensed on a condenser surface **19** disposed above the support structure **30**. Preferably the condenser surface **19** is movable and, as illustrated, the condenser surface **19** is rotatably mounted in the wall **24** and the end wall of the housing **11**. The condenser surface is cooled, as by a suitable fluid such as water or gas introduced through a concentric pipe **21** and is rotated by a suitable motor M.

Preferably, the raw material feedstock is melted and forms a molten pool of reactants in the preheat region **18**. If the raw materials are contained in metal boxes as set forth above, the boxes preferably are made from a metal that will also be melted in the preheat region **18**. The molten reactants flow into the purification region through a slot **26** formed in the wall **24**. In conjunction with this, the molten reactants are retained in the preheat region a sufficient length of time to effect substantial vaporization of the volatile impurities and reducing agent compounds that are vaporizable at the operating pressure and temperature of the preheat region before being delivered through slot **26** into the purification region **20**.

The molten reactants flow through slot **26** into a hearth **34**. The hearth **34** can be made from any convenient material, e.g., copper, and is usually water cooled, which causes the formation of a solidified liner **35** of the reactants to be formed on the surface of the hearth. The hearth **34** is formed with a series of baffles **36** which are arranged to provide a sinuous path, as shown in FIGURE 1, to provide for a longer period of travel of the reactants through the purification chamber.

The molten reactants are further heated in the purification chamber at a higher vacuum than that obtained in the preheat region **18**, e.g., less than about 2 microns of mercury and, preferably, about 0.5 micron of mercury or less, with electron beam guns, substantially the same as described above, which are arranged within a housing **38**, similar to housing **29**, disposed to one side of hearth **34**. The housing **38** is connected by pipes **38***a* to the vacuum diffusion pumps (not shown). The electron guns within housing **38** are suitably arranged so that the electron beams follow a curved path onto the surface of the molten reactants within hearth **34** as shown in FIGURE 3. The electron beam causes convection currents to be set up within the molten pool, and new reactants are constantly brought to the surface of the molten pool.

The electron guns within housing **38** may be suitably adjusted so that the temperature of the molten bath within the hearth **34** is progressively increased from entrance to exit in order that the molten metal product will leave the purification region at a temperature such that substantially all of the reducing agent will be vaporized therefrom without any appreciable vaporization of the desired metal product. Preferably, the temperature is raised to slightly above the melting point of the desired metal product at the operating conditions.

If desired, the apparatus may be suitably modified to practice a batch process. In such a process the temperature within the purification region **20** is desirably adjusted so that an initial temperature is maintained at which the reactants are maintained in a molten state and at which the remainder of the remaining reducing agent compounds formed during the reduction reaction are vaporized. The temperature is then slowly raised to a point where substantially all of the reducing agent will be vaporized without and appreciable vaporization of the desired metal product, e.g., just above the melting point of the metal product. As the temperature is raised, any remaining unreacted re-

ducing agent present in the molten bath is vaporized and the metal employed as a container for the raw materials, if any, vaporizes, leaving a highly purified molten bath of the product metal. Depending upon the properties of the particular reducing agent, and the volatility of the reducing agent compared to the product metal at the operating conditions, the reducing agent may be vaporized either in elemental or in combined form.

As shown in FIGURE 1, a rotatable condenser surface 39, similar to the condenser surface 19 is disposed in the preheat region 18, is rotatably mounted in walls 24 and 25 directly above the hearth 34. The condenser surface 39, which can be constructed of any suitable material, is cooled by suitable means such as a coolant gas or liquid introduced and withdrawn through a concentric pipe 47. The concentric pipe 47 may be connected by suitable means to the concentric pipes 21 in order that both condensers 19 and 39 may be cooled by a single source. If desired, the condenser 39 may be connected by suitable means to condenser 19 so that the motor M may be used to rotate both condenser 19 and condenser 39. Alternately, other forms of condensers, such as a moving metal sheet may be used in place of the rotating drum.

The condenser 39 is maintained at a temperature which is low enough to condense the reducing agent and reducing agent compound vapors on its surface, as well as the majority of the other condesible impurities which may be present, but which will not condense any of the highly volatile impurities which may be present in the feed raw material. The noncondensibles, e.g., carbon monoxide and nitrogen, formed during the purification process, are withdrawn from the furnace by the diffusion pumps through the manifold 28.

The product metal remaining after the reducing agent and reducing agent compounds have been vaporized is passed out of the hearth 34 through a slot in the wall 25 and is delivered to a direct chill ingot mechanism 46 maintained in the product withdrawal region 22 of the furnace 10. The metal product may be heated by an electron gun, similar in structure to the electron guns described above, maintained within the housing 49 and connected by pipe 49a to suitable vacuum pumps in order to maintain the product metal in a molten condition in the upper portion of the ingot mold 46. The ingot mechanism is cooled, as by suitable water coils 48, causing the solidification of the metal product within the ingot mechanism. The solidified ingot passes out of the furnace 10 through a conventional means for withdrawing ingots from a vacuum system, indicated generally by numeral 50.

The reducing agent, reducing agent compounds and other impurities condensed upon the condenser surface 39 are removed therefrom in the form of chips or flakes by any convenient means, such as a scraper blade 54, (FIGURE 3), and are collected in a vacuum lock indicated generally at 56 where they are periodically removed from the furnace. In a like manner the condensed materials are removed from the condenser surface 19 through another suitable vacuum lock (not shown). The condensed materials thus obtained can be discarded or can be chemically treated to recover any metal product that might be vaporized and condensed on the condenser.

The mechanism by which the reducing agent is vaporized from the molten reactants in the electron beam furnace is dependent upon the volatility of the reducing agent at the operating conditions. If a reducing agent such as aluminum is employed which is substantially more volatile than the desired metal product at the operating conditions within the electron beam furnace, it may be possible to vaporize substantially all of the aluminum from the desired metal product as aluminum vapor without substantially vaporizing any of the metal product, leaving a metal product that is substantially free from aluminum, e.g., a product containing 100 p.p.m. aluminum or less.

Other reducing agents that may be employed, e.g., silicon, have a volatility at the operating conditions that is close to the volatility of the desired metal product. In such instances it is not feasible to vaporize all of the reducing agent from the desired metal product in elemental form. The silicon is eliminated from the metal product by employing an amount of silicon that is less than the stoichiometric amount required to react with all of the oxygen impurity in the raw material oxide ore. When less than a stoichiometric amount of silicon is employed as the reducing agent, the vaporization of substantially all of the silicon as silicon monoxide is assured. The oxygen remaining in the molten reactants after substantially all of the silicon monoxide has vaporized combines with the desired metal product to form an oxide, e.g., columbium monoxide, tantalum monoxide, etc., which is more volatile than the desired metal product at the operating conditions and which is readily vaporized from the desired metal product leaving a highly purified molten pool of the desired metal.

If, for some reason, an excess of the reducing agent or carbon is found to be present in the product metal after the purification process has been carried out which cannot be completely vaporized at the operating conditions, oxygen may be injected or bled into the purification region. The oxygen reacts with the reducing agent and/or carbon to form volatile oxides which are vaporized from the product metal at the operating conditions.

If it is desired that the purified metal product be substantially free from carbon, an amount of reducing agent correspondingly less than the stoichiometric amount is employed. In this instance there will be oxygen in combined form remaining after all of the reducing agent has been vaporized in the form of reducing agent compounds with which the carbon can react to form carbon monoxide which is vaporized from the molten reactants at the operating conditions.

Alloys of the various metals which can be purified by the foregoing process can be formed by mixing together various amounts of the oxide ores of the desired metals. The reducing agent is then admixed with the combined metal oxides and the reduction is effected in the electron beam furnace in the manner as previously described, the amount of reducing agent employed being chosen to react with all of the oxygen present in each of the metals which form the purified alloy product.

If a highly purified metal product of a single metal is desired, all of the metals which are set forth as being capable of being purified by the process described are preferably removed from the raw materials charged into the electron beam furnace as the process is not designed to separate these metals from one another. For instance, if a highly purified tantalum metal is desired, columbium, which is invariably associated with tantalum ores, must be removed before the purification process is initiated. However, there are conventional chemical separation processes, such as liquid-liquid extraction, which are available to those skilled in the art for separating tantalum from columbium, as well as for separating other metals when present in a combined form, and it is not considered to present a problem to separate the crude ores of the desired metal products before the purification process is initiated.

In some instances an analysis of the condensed reducing agent compounds scraped from the condenser surface will show that a measurable amount of the desired product metal was carried over by the distilled vapors. In these cases the desired metal can be recovered from the condensed materials by conventional crude ore recovery processes and recycled back to the furnace as a raw material.

The process as previously described may be employed in the production of highly purified metals by direct reduction, i.e., a process wherein the raw material feed-

stock is introduced directly into the electron beam furnace; or by a two-stage process wherein the raw material feedstock is first reduced in an atmospheric stage at a pressure well above the reduced pressure required for electron beam purification, e.g., at atmospheric pressure according to conventional practices, followed by the further purification of the crude intermediate product obtained from the atmospheric stage in a vacuum stage in an electron beam furnace according to the procedures set forth above.

In a conventional atmospheric pressure reduction process the raw material feedstock is reduced at substantially atmospheric pressure utilizing a suitable reducing agent, e.g., aluminum, silicon, etc., or other suitable thermite or electric furnace type reducing agent. The oxide impurities produced in the atmospheric reduction process are slagged off as aluminates, silicates, etc., by the addition of suitable slagging agents, e.g., lime, leaving a partially purified crude intermediate metal product. The crude intermediate product thereby obtained may be introduced into the electron beam furnace for further melting and purification.

The use of a two-stage process for the production of highly purified metals is advantageous in that the atmospheric stage purification removes a substantial portion of both the condensible and the noncondensible volatile materials from the raw material feedstock. When the raw material feedstock is introduced directly into the electron beam furnace in a direct reduction process the noncondensible volatile materials must be removed from the furance by the pumping action of the vacuum pumps, and the volatile condensible materials must be condensed upon and scraped from the condenser surface. However, when a substantial portion of these materials are removed from the raw material feedstock prior to its introduction into the electron beam furnace, the pumping capacity of the vacuum pumps may be accordingly reduced. At the same time the amount of volatile condensible materials entering the electron beam furance is accordingly reduced since a substantial portion of these materials are removed in the atmospheric stage as slag. Further, when the raw material feedstock is directly reduced in the electron beam furnace the reducing agent oxides that are formed and vaporized are monoxides whereas the oxides in the atmospheric reduction process are the normal oxides, e.g., dioxides and trioxides. It can be seen that a lesser amount of reducing agent can be employed to purify a given amount of raw material feedstock in a two-stage purification process, representing a substantial reduction in the cost per pound of the highly purified metal product.

In a two-stage purification process the melting point of the crude intermediate product obtained from the atmospheric stage may be suitably adjusted by the addition of certain volatile metals. For example, in the aluminum reduction of columbium in a two-stage reduction process approximately 10 percent by weight excess aluminum in the crude columbium intermediate product lowers the melting point of that product to about 1800° C., to about 2000° C. The excess aluminum readily vaporizes from the crude columbium when it is melted in the electron beam furnace, and the presence of aluminum in the crude columbium product has no significant effect on either the pumping capacity of the vacuum pumps in the electron beam furnace or the production rate of highly purified columbium obtained from the electron furnace. The lowering of the melting point of the crude intermediate product is advantageous in that it aids in preventing violent eruptions and/or splattering of the crude intermediate product during the initial melting thereof in the preheat region of the electron beam furnace.

The use of aluminum to lower the melting point of the crude intermediate product also aids in eliminating the pickup of silicon or other impurity metals from the ceramic bricks used in the reduction or casting steps in the atmospheric stage which may occur if it is necessary to employ higher temperatures in order to maintain a molten pool of reactants in the atmospheric stage. Similarly, in the use of a silicon reducing agent in an atmospheric stage reduction, iron may be added to lower the melting point of the crude intermediate product. When a ferroalloy is employed as a raw material feedstock sufficient iron will normally be present in the feedstock so that additional iron is not needed.

It is also advantageous to employ ceramic bricks or refractory materials in the atmospheric reduction process that do not contain silicon, silica or silicate, since these materials may be picked up from the bricks by the crude intermediate product as described. Instead, alumina or aluminate bricks are preferably employed in order to be sure that the crude intermediate product will contain as small amount of silicon as possible. However, as stated above, when the melting point of the crude intermediate product is suitably adjusted, it may be possible to employ apparatus in the atmospheric stage reduction process that contain silicon ceramic bricks or the like.

The atmospheric stage reduction process desirably should be carried out so that the crude intermediate product contains only minor amounts of volatile noncondensible materials such as nitrogen and carbon which must be eliminated from the crude intermediate product as nitrogen gas and carbon monoxide gas by the action of the vacuum pumps in the electron beam furnace. Commercially available metals purified in an atmospheric stage reduction process contain about 0.1 percent nitrogen and about 0.1 to about 0.2 percent carbon. However, the presence of nitrogen and carbon in these amounts causes the formation of excessive amounts of noncondensible nitrogen and carbon monoxide gas which must be removed from the electron beam furnace by the vacuum pumps. It has been found that if both the nitrogen and carbon content of the crude intermediate product are maintained below 0.05 percent by weight the amount of noncondensible gas formed will be substantially reduced and the economics of the process will be enhanced. By suitably adjusting the atmospheric reduction process according to known practices, a crude intermediate product may easily be obtained having nitrogen and carbon contents below the above specified amounts.

If silicon is employed as the reducing agent in the atmospheric stage reduction process, a deficiency of silicon is desirably employed in order to produce a crude intermediate product containing a greater amount of oxygen than silicon. Preferably, the crude intermediate product contains at least 0.1 weight percent oxygen, generally 0.2 to 0.50 percent and less than 0.1 weight percent silicon. Greater amounts of oxygen may be tolerated, but result in the loss of greater amounts of the desired metal product due to vaporization of an oxide thereof. When a crude intermediate product containing silicon and oxygen in the above specified amounts is melted in an electron beam furnace in the vacuum purification stage, any remaining silicon reacts with the oxygen and is vaporized as silicon monoxide. The oxygen remaining after substantially all of the silicon has been vaporized reacts with the metal product and is vaporized as an oxide, e.g., columbium oxide, thereby providing a purified metal product that is substantially free of silicon and oxygen. If more silicon is present in the crude intermediate product than oxygen, as when certain raw material ores are employed, the silicon may be removed from the desired metal product in the electron beam furnace by the injection or bleeding of oxygen into the purification region of the electron beam furnace as previously described.

The crude intermediate product obtained from the atmospheric stage reduction is fed into the electron beam furnace in large pieces or as small shapes or flakes which are contained in iron boxes, as may be desired and is

further purified according to the above described process. When a crude intermediate product having the properties specified above is introduced into the preheat region of the electron beam furnace, the crude product melts with very little splatter and evolves the volatile materials therein quite rapidly. In such instances the crude intermediate product may contain up to 30 to 50 atomic weight percent condensible volatile materials.

If a metal alloy product is desired, the appropriate oxide mixture may be formulated as a raw material feedstock and fed into the atmospheric stage reduction apparatus. The crude intermediate alloy product is then introduced into the electron beam furnace and further purified as described. If the desired alloy contains metals which form volatile suboxides, e.g., columbium base alloys containing zirconium, the atmospheric stage reduction should be carried out in a manner which provides a very low atomic weight percent oxygen content in the crude intermediate product. The use of an aluminum reducing agent in a thermite reduction process wherein the crude intermediate product contains 10 weight percent aluminum is particularly suitable for the production of alloys of metals which form volatile suboxides. If the alloying metals are chemically more reactive than the base metal, e.g., columbium base alloys containing tantalum, the slag obtained from the atmospheric pressure reduction process will contain a higher ratio of tantalum to columbium than does the initial raw material feedstock. Thus, the raw material feedstock must be compensated for the presence of tantalum in the slag. The tantalum that is carried off by the slag may be recovered through the use of an acid recovery step.

Various features of the method as described are set forth in the following examples.

Example I

High purity columbium is produced from powdered columbium oxide concentrates containing 92 percent columbium oxide, the remainder being mainly silicon dioxide, oxides of iron and other metals by mixing finely divided silicon with the columbium oxide and reacting the mixture in an electron beam furnace. The silicon is added in an amount slightly less than 5 moles of silicon per mole of columbium oxide and 1 mole of silicon per mole of silicon dioxide to provide a deficiency of silicon. Other residual metal oxides, such as iron oxide, are also compensated for by the addition of slightly less than 1 mole of silicon per mole of oxygen present and the mixture is briquetted and placed in sheet iron boxes, and charged into the preheat section of an electron beam furnace.

The preheat section of the electron beam furnace is maintained at a reduced pressure of about 100 microns of mercury by vacuum diffusion pumps and at a temperature of about 1500° C. by electron guns at which temperature and pressure the reaction proceeds spontaneously in the solid mixture of the columbium oxide and silicon and the feedstock begins to melt. The temperature is slowly raised to 1800° C. to maintain a molten pool of the reactants and silicon monoxide vapors are evolved from the molten pool and condensed on the surface of a rotating condenser surface positioned directly above the molten pool. When the temperature of the molten pool reaches 1800° C. about two-thirds of the silicon monoxide capable of being formed and vaporized from the molten pool of raw material feedstock is vaporized.

The molten reactants at 1800° C. flow into the purification region of the electron beam furnace which is maintained at reduced pressure of about 0.1 micron Hg. The electron beam heating of the reactants causes the remaining silicon monoxide to vaporize from the molten pool. The temperature of the reactants is increased as they flow through the hearth in order to maintain a molten pool. The temperature of the molten pool is increased to approximately 2600° C., adjacent the exit from the purification region which is about 50° C. above the melting point of pure columbium. At this temperature the iron present in the reactants vaporizes from the molten pool. The slight deficiency in the stoichiometric amount of silicon is such that the evolution of silicon monoxide at 2600° C. will reduce the silicon content of the product metal to less than 50 p.p.m. The oxygen content of the product metal is reduced to less than 50 p.p.m. by vaporization of columbium monoxide after the silicon monoxide has vaporized.

The various condensible materials vaporized in the purification region are condensed on a rotating condenser surface and are scraped from the condenser surface and removed from the furnace. The thus condensed residue is treated with hydrofluoric acid to recover the columbium carried over during the purification process, the recovered columbium being recycled back through the furnace as raw material.

The purified molten columbium metal is delivered from the purification region into the product withdrawal region of the furnace where it is further heated with an electron beam and continuously cast in a cooled ingot mold mechanism. The ingot is continuously withdrawn from the electron beam furnace through a vacuum lock and cut into suitable shapes.

The columbium metal product obtained analyzes less than 50 p.p.m. of oxygen, 20 p.p.m. of nitrogen, 5 p.p.m. of hydrogen, 75 p.p.m. of carbon, 50 p.p.m. of silicon and 50 p.p.m. of iron.

Example II

High purity tantalum is produced in an electron beam furnace by a batch process from tantalum ores by extracting the columbium concentrates from the tantalum ores with a hydrofluoric acid leeching process and admixing the tantalum oxide raw material obtained from the leeching process with silicon metal in the ratio of 5 moles of silicon per mole of tantalum oxide. As is the case in the previous example amounts of silicon are added to compensate for the presence of other impure metal oxides within the raw material on a mole to mole basis and the mixture of tantalum oxide and silicon is briquetted in a similar manner to that employed in Example I and charged to the electron beam furnace in sheet iron boxes.

The process is carried out in a manner similar to that of Example I, the raw materials being heated to about 1800° C. in the preheat section of the furnace to form a molten pool and to cause vaporization of about two-thirds of the silicon monoxide available from the raw material feed-stock. The molten reactants at 1800° C. are charged into the purification region of the furnace and are further heated at a pressure of 0.1 micron of mercury.

The temperature within the purification region is raised to slightly above the melting point of pure tantalum at the operating conditions, i.e., 2900° C. to 3000° C., with the vaporization of the iron, the remaining silicon monoxide, tantalum oxide and other remaining metallic impurities, leaving a molten purified tantalum bath. The impurities vaporized in the preheat and purification regions of the furnace are condensed on a rotating condenser surface in a manner as described and are removed from the furnace.

The purified tantalum is then delivered into a water cooled ingot withdrawal mechanism as described where it is cast and withdrawn from the furnace.

The purified tantalum product analyzes less than 20 p.p.m. oxygen, 10 p.p.m. nitrogen, 1 p.p.m. hydrogen, 10 p.p.m. iron, 30 p.p.m carbon, and 30 p.p.m. silicon.

Example III

A highly purified tantalum product was attained in a manner similar to that employed in Example II in a continuous manner by adjusting the electron beam guns striking the surface of the molten bath within the puri-

fication region so that the temperature of the bath is increased from about 2000° C. adjacent the point at which the raw materials enter the purification region to a temperature of 2950° C., i.e., just above the melting point of tantalum at the operating pressure, adjacent the exit of the purification region.

The tantalum oxide ore is purified in the manner described. A product was obtained employing the continuous process which analyzed less than 20 p.p.m. oxygen,, 10 p.p.m. nitrogen, 1 p.p.m. hydrogen, 10 p.p.m. iron, 30 p.p.m. carbon and 30 p.p.m. silicon.

Example IV

A highly purified alloy of 50 mol percent columbium and 50 mol percent tantalum is produced by forming a mixture of equimolar amounts of columbium oxide and tantalum oxide and admixing silicon therewith, 5 moles of silicon being employed for each mole of columbium oxide and each mole of tantalum oxide. The mixture of oxides and silicon is charged into an electron beam furnace in iron boxes in a manner similar to that described in Example I, and is melted in the preheat region of an electron beam furnace at a pressure of 100 microns of mercury and a temperature of 1500° C., the temperature being slowly raised to 1800° C. with the evolution of silicon monoxide which is condensed on a cooled condenser surface. The molten mass of columbium and tantalum silicide obtained in the preheat region is then charged into the purification region of the furnace at a temperature of 1800° C. and at a pressure of 0.1 micron of mercury. As the molten reactants flow through the hearth, the temperature is raised to 2800° C., slightly above the melting point of the pure columbium-tantalum alloy. At a temperature of 2800° C., the iron, remaining silicon monoxide and some columbium oxide and tantalum oxide vaporize from the molten pool leaving a highly purified molten alloy of columbium and tantalum which is withdrawn from the furnace through the cooled ingot mechanism as described in the preceding examples.

The columbium-tantalum alloy analyzed less than 35 p.p.m. oxygen, 15 p.p.m. nitrogen, 3 p.p.m. hydrogen, 30 p.p.m. iron, 50 p.p.m. carbon and 65 p.p.m. silicon.

Example V

Highly purified columbium is produced from a columbium oxide ore in a two-stage purification process. In a first atmospheric reduction stage the columbium oxide is reduced with a sufficient amount of aluminum to provide a crude intermediate columbium product containing 10 weight percent aluminum, about 0.03 percent nitrogen and 0.03 percent carbon. The crude intermediate product is introduced into an electron beam furnace and is melted in a preheat region within the furnace at a temperature of 1800° C. accompanied by the vaporization of aluminum and aluminum monoxide. The vaporization of the volatile materials is accomplished with very little splatter. The pressure within the preheat region of the electron beam furnace is maintained at between 5 microns and 10 microns of mercury.

The molten columbium containing reactants are then introduced into the purification region of the electron beam furnace and further purified according to the process described in Example I.

A columbium metal product is obtained which analyzes less than 50 p.p.m. oxygen, 20 p.p.m. nitrogen, 5 p.p.m. hydrogen, 75 p.p.m. carbon, 100 p.p.m. aluminum, 50 p.p.m. iron and 50 p.p.m. silicon.

Example VI

Highly purified tantalum is produced from tantalum oxide ores in a two-stage purification process. The tantalum oxide ores are reduced in a first atmospheric reduction stage with an amount of silicon that is less than the stoichiometric amount required to react with all of the oxygen in the raw material oxide ore. The atmospheric stage reduction process is carried out so that a crude intermediate tantalum product is obtained which contains about 0.09 weight percent silicon, about 0.03 weight percent nitrogen, 0.3 weight percent oxygen and 0.03 weight percent carbon. The crude intermediate tantalum product is further purified in a vacuum reduction stage in an electron beam furnace according to the method of Example II.

The purified tantalum product analyzes less than 20 p.p.m. oxygen, 10 p.p.m. nitrogen, 1 p.p.m. hydrogen, 10 p.p.m. iron, 30 p.p.m. carbon, 30 p.p.m. silicon and 20 p.p.m. aluminum.

It can be seen that a process has been provided which produces metals and metal alloys in a higher degree of purity than has heretofore been obtainable and does so in either a batch or a continuous process which is both economical and convenient It is understood that other metals, such as tungsten, molybdenum, zirconium, hafnium and rhenium, and others whose partial pressures at high vacuums are such that their oxide ores can be reacted with a reducing agent to produce more volatile reducing agent compounds separable by vaporization techniques can be purified by the disclosed process and are within the scope of the invention.

Various of the features of the present invention are set forth in the following claims.

What is claimed is:

1. The method of producing a highly purified metal or alloy selected from the group consisting of columbium, tantalum, molybdenum, tungsten, hafnium, zironium and rhenium from a mixture of an oxide of said metal and a reducing agent selected from aluminum and silicon, comprising reacting said mixture at reduced pressure of not more than about 2 microns of mercury and at an elevated temperature in an electron beam furnace to form reducing agent oxides, said reducing agent oxides being more volatile than said metal at said pressure and said temperature, vaporizing said reducing agent oxides from said metal and recovering said metal in a purified form.

2. The method of producing a highly purified metal or alloy selected from the group consisting of columbium, tantalum, molybdenum, tungsten, hafnium, zirconium and rhenium from a mixture of an oxide of said metal and a reducing agent selected from the group consisting of silicon and aluminum comprising, reacting said mixture in a first region of an electron beam furnace to produce reducing agent oxides at a reduced pressure of about 1 micron to about 500 microns of mercury and at an elevated temperature sufficient to vaporize a major portion of said reducing agent oxides at said pressure but insufficient to vaporize a substantial amount of said metal, further reacting said mixture in a second region of said furnace at a pressure of not more than about 2 microns of mercury and at a higher temperature sufficient to vaporize substantially all of said reducing agent oxides remaining in said mixture but insufficient to vaporize a substantial amount of said metal, said reducing agent oxides being more volatile than said metal at said pressures and said temperatures, and recovering said metal in a purified form.

3. The method of producing a highly purified metal or alloy selected from the group consisting of columbium, tantalum, molybdenum, tungsten, hafnium, zirconium and rhenium from a mixture of an oxide of said metal and a silicon reducing agent, said silicon being present in an amount less than the stoichiometric amount necessary to combine with all of the oxygen of said metal oxide comprising, reacting said mixture in an electron beam furnace to form silicon oxides at a reduced pressure of not more than 2 microns of mercury and at an elevated temperature sufficient to vaporize said silicon oxides but insufficient to

vaporize a substantial amount of said metal, said silicon oxides being more volatile than said metal at said pressure and said temperature, reacting the remaining of the oxygen present in said mixture with said metal to form a metal monoxide, said metal monoxide being more volatile than said metal at said pressure and said temperature vaporizing said metals monoxide without substantially vaporizing said metal and recovering said meal in purified form.

4. The method of producing a highly purified metal or alloy selected from the group consisting of columbium, tantalum, molybdenum, tungsten, hafnium, zirconium and rhenium from a mixture of an oxide of said metal and a silicon reducing agent, said silicon being present in an amount less than the stoichiometric amount necessary to combine with all of the oxygen of said metal oxide comprising, reacting said mixture in a first region of an electron beam furnace to produce silicon oxides at a reduced pressure of about 1 micron to about 500 microns of mercury and at an elevated temperature sufficient to vaporize a major portion of said silicon oxides but insufficient to vaporize a substantial amount of said metal, further reacting said mixture in a second region of said furnace at a pressure of not more than about 2 microns of mercury and at a higher temperature sufficient to vaporize any remaining of said silicon oxides but insufficient to vaporize a substantial amount of said metal, said silicon oxides being more volatile than said metal at said pressures and said temperatures, reacting the remaining of the oxygen present in said mixture with said metal to form a metal monoxide at said second pressure and at a temperature sufficient to vaporize substantially all of said metal monoxide but insufficient to vaporize a substantial amount of said metal, and recovering said metal in a purified form.

5. The method of producing a highly purified metal or alloy selected from the group consisting of columbium, tantalum, molybdenum, tungsten, hafnium, zirconium and rhenium from a mixture of an oxide of said metal and an aluminum reducing agent, which method comprises reacting said mixture in a first region of an electron beam furnace to produce aluminum oxides at a first pressure within the range of about 1 micron of mercury to about 500 microns of mercury and at a temperature sufficient to vaporize a major portion of said aluminum oxides but insufficient to vaporize a substantial amount of said metal, further reacting said mixture in a second region of said furnace at a pressure of not more than 2 microns of mercury, and at a temperature sufficient to vaporize substantially all of any remaining of said aluminum oxides without vaporizing a substantial amount of said metal, vaporizing any remaining unreacted aluminum in said second region at said second pressure and at a temperature sufficient to vaporize substantialy all of said aluminum without vaporizing a substantial amount of said metal, and recovering said metal in purified form.

6. The method of producing a highly purified metal or alloy selected from the group consisting of columbium, tantalum, molybdenum, tungsten, hafnium, zirconium and rhenium from a mixture of an oxide of said metal and a reducing agent capable of reducing said metal oxide, which method comprises the steps of first reacting said mixture at ambient pressure and at an elevated temperature to form reducing agent oxides and separating said reducing agent oxides to provide a crude intermediate metal product, heating said intermediate product in an electron beam furnace at a pressure of not more than 2 microns of mercury and at a temperature sufficient to vaporize any remaining of said reducing agent oxides present in said intermediate product without vaporizing a substantial amount of said metal, and recovering said metal in purified form.

7. The method of producing a highly purified metal or alloy selected from the group consisting of columbium, tantalum, molybdenum, tungsten, hafnium, zirconium and rhenium from a mixture of an oxide of said metal and a reducing agent capable of reducing said metal oxide, which method comprises the steps of first reacting said mixture at ambient pressure and at an elevated temperature to form reducing agent oxides and separting said reducing agent oxides to provide a crude intermediate metal product, said intermediate product containing less than about 0.05 percent nitrogen and less than about 0.05 percent carbon, heating said intermediate product in a first region of an electron beam furnace at a reduced pressure of about 1 micron to about 500 micons of mercury and at an elevated temperature sufficient to vaporize a major portion of any remaining of said reducing agent oxides present in said intermediate product but insufficient to vaporize a substantial amount of said metal, further heating said intermediate product in a second region of said furnace at a pressure of not more than about 2 microns of mercury and at a higher temperature sufficient to vaporize substantially all of said reducing agent oxides but insufficient to vaporize a substantial amount of said metal, said reducing agent oxides being more volatile than said metal at said pressures and said temperatures, and recovering said metal in a purified form.

8. The method of producing a highly purified metal or alloy selected from the group consisting of columbium, tantalum, molybdenum, tungsten, hafnium, zirconium and rhenium from a mixture of an oxide of said metal and a reducing agent capable of reducing said metal oxide, which method comprises the steps of first reacting said mixture at ambient pressure and at an elevated temperature to form reducing agent oxides, separating said reducing agent oxides to provide a crude intermediate metal product containing an excess of unreacted reducing agent, less than about 0.05 percent nitrogen and less than 0.05 percent carbon, heating said intermediate product in a first region of an electron beam furnace at a reduced pressure of about 1 micron to about 500 microns of mercury and at an elevated temperature sufficient to vaporize a major portion of any remaining of said reducing agent oxides present in said intermediate product and a portion of said unreacted reducing agent but insufficient to vaporize a substantial amount of said metal, further heating said mixture in a second region of said furnace at a pressure of not more than about 2 microns of mercury and at a higher temperature sufficient to vaporize substantially all of the remaining of said reducing agent oxides and said unreacted reducing agent but insufficient to vaporize a substantial amount of said metal, and recovering said metal in a purified form.

9. The method of producing a highly purified metal or alloy selected from the group consisting of columbium, tantalum, molybdenum, tungsten, hafnium, zirconium and rhenium from a mixture of an oxide of said metal and silicon, which method comprises the steps of first reacting said mixture at ambient pressure and at an elevated temperature to provide a crude intermediate metal product, said intermediate product comprising at least about 0.1 percent oxygen, less than about 0.1 percent silicon, less than about 0.05 percent nitrogen and less than about 0.05 percent carbon, reacting said intermediate product in an electron beam furnace at a reduced pressure of not more than about 2 microns of mercury and at an elevated temperature sufficient to substantially vaporize residual reducing agent oxides but insufficient to vaporize a substantial amount of said metal, reacting the remaining of the oxygen present in said mixture with said metal to form a metal monoxide at said pressure and at a temperature sufficient to substantially vaporize said metal monoxide but insufficient to vaporize a substantial amount of said metal and recovering said metal in purified form.

10. The method of claim 2 wherein said metal is columbium.

11. The method of claim 2 wherein said metal is tantalum.

12. The method of claim 2 wherein said metal is molybdenum.

13. The method of claim 2 wherein said metal is tungsten.

14. The method of claim 2 wherein said metal is hafnium.

15. The method of claim 2 wherein said metal is zirconium.

16. The method of claim 2 wherein said metal is rhenium.

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