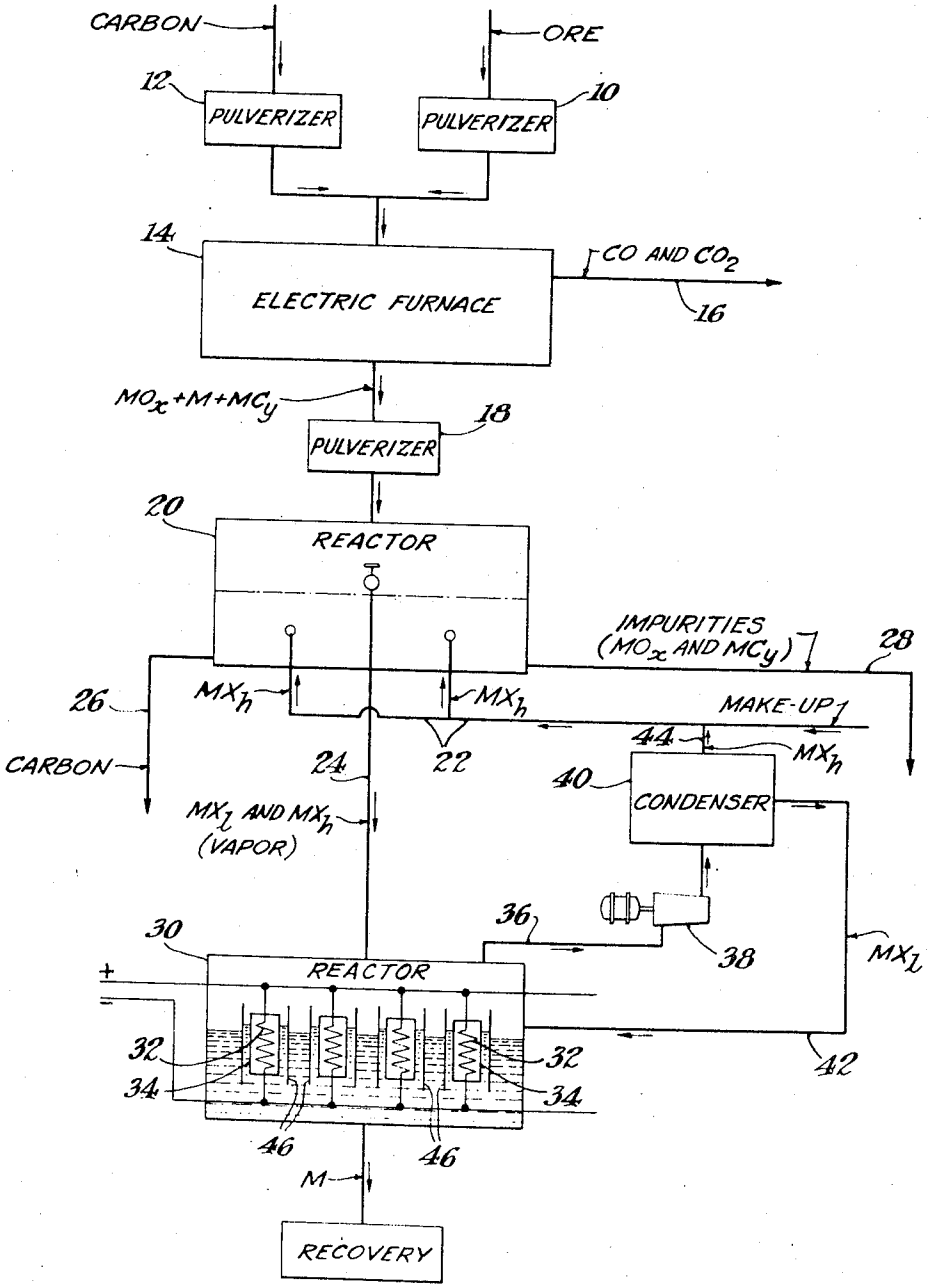
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METHOD OF REFINING METALS

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METHOD OF REFINING METALS

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This invention relates to the production of high melting point metallic elements and has for an object the provision of an improved method or process for producing high-purity refractory metals. More particularly, the invention contemplates the provision of an improved method or process for producing high-purity, high melting point metallic elements, including titanium, zirconium, tungsten, hafnium and uranium, by the disproportionation of lower bromides of such elements. This application is a continuation-in-part of our copending application Serial Number 575,792, filed April 3, 1956, and entitled "Method of Refining Metals."

Titanium, zirconium, tungsten, hafnium and uranium have become important commercial materials in view of the unusual properties which they exhibit. At present, there are several ways of recovering such metals all of which are complicated and expensive. For instance, the procedures now used for the manufacture of titanium are the following:

(1) Reduction of titanium tetrachloride or other titanium tetrahalide with either sodium or magnesium with subsequent elimination of the sodium or magnesium halide which is formed by washing or distillation.

(2) Reduction of titanium oxide with calcium hydride at elevated temperature. This procedure has not been too successful since the product is always heavily contaminated with oxygen.

(3) Thermal dissociation of a titanium tetrahalide on a hot filament under vacuum.

(4) Electrolytic recovery from fused salts.

At the present time, the most widely used commercial method is the reduction of titanium tetrachloride with magnesium or sodium followed by subsequent distillation of the magnesium chloride or sodium chloride by-product in a vacuum. This process, popularly referred to as the Kroll process, is inherently expensive since it produces a titanium halide from a titanous ore and then reduces the halide with another substantially pure metal. In such a process, the necessary expense of the pure secondary metal establishes a very high minimum cost. Also the titanium is formed as a metallic sponge which necessitates further processing to obtain the metal in a useable form.

As indicated, titanium, as well as the other aforementioned metals, have many unusual physical and chemical properties. In order to be workable and generally useful, these metals have to be supplied in an extraordinarily pure form. Small percentages of oxygen, nitrogen, hydrocarbon or carbon embrittle the metal markedly so that it cannot be handled by conventional metal working procedures. Under these conditions, great care is taken to eliminate these undesirable elements from being present while the metal is being formed. While the above noted processes are illustrative of titanium recovery, they are in principle applicable to other metal recovery in pure elemental form. These processes usually involve the recovery of crystalline metals in the form of extremely small particles or a sponge form of metal. The small particles are inherently unstable and even pyrophoric, readily oxidizing in the presence of air or water, and even react with nitrogen from the air to form nitrides of the metal.

Other difficulties with the treatment and recovery of these metals result from their high melting point. The

property of titanium, in the molten state, of acting as a nearly universal solvent presents a major problem in handling the metal in such a state. Almost all of the impurities tolerable in other materials reduce the ductility of the high melting point metals to the degree of being unworkable.

To illustrate our process of producing high purity, high melting point, metallic elements we have hereinafter described our invention with regard to the treatment and recovery of titanium.

In accordance with the present invention, the metal titanium is produced as a relatively high purity product of the little known reaction of titanium monoxide with the titanium halides. Although the reactions of decomposition of sub-halides to metal and higher halides has been known, the possibilities of combined titanium halide reactions have not been appreciated. Through our invention pure ductile titanium is produced in plate or ingot form, rather than in oxidizable crystals or sponge form, and at a cost substantially below that of present day methods. Further, our invention provides a relatively low temperature process which can operate at substantially atmospheric pressure with a minimum of heat input and without the need for hydrogen or other costly reducing materials such as sodium or magnesium. Other objects and advantages of our invention will appear from the following description of one form of embodiment taken in connection with the attached drawing which is a simplified flow diagram of the reaction according to the invention.

In view of the various metals recoverable and variations of equipment which may be used to carry out our our process, the flow diagram is to be considered of generally informative nature and illustrative of process steps rather than a limitation as to a specific metal or type of apparatus.

Accordingly, in our method, titanium bearing ores such as rutile, ilmenite and titanite or titanium dioxide-bearing slag obtained as a result of the smelting of titaniferous iron ore, are charged to pulverizer 10. These ores or slag, even in their purest state, contain iron, silicon and aluminum as regular impurities. Alkaline earth metals, such as calcium, are likewise commonly found in various titania rich ores. We reduce the titanium dioxide of such ores with powdered carbon supplied to pulverizer 12 and produce titanium contaminated with lower oxides including Ti_3O_5, Ti_2O_3 and TiO, and titanium carbide in furnace 14. The reducing agent fed to pulverizer 12 may be derived from any known carbon source; however, in order to limit contamination of the lower oxides of titanium, we prefer to employ petroleum coke or charcoal. The carbon in the mixture serves primarily to remove the oxygen from the titanium dioxide in the form of carbon monoxide and carbon dioxide, thereby reducing the titanium dioxide to titanium. Some of the carbon may react with the titanium dioxide to form titanium carbide and carbon monoxide and carbon dioxide. To prepare titanium in furnace 14, we have used a mixture of 80 parts by weight of crushed rutile and 27 parts by weight of crushed petroleum coke, consolidated by pressure to a dense solid. Analysis of the rutile and petroleum coke used by us indicated the following.

Rutile:

	Percent
TiO_2	93.20
Fe_2O_3	1.73
SiO_2	2.03
Al_2O_3	0.70
CaO	1.74
P_2O_5	0.60
	100.00

Petroleum coke:	
Volatile matter	8.81
Fixed carbon	89.86
Ash	1.33
	100.00

The furnace 14 may be an electric resistance furnace or it may be of any typical arc, cupola or fluidized design. In the furnace, the titanium dioxide is reduced by carbon by a series of step-wise reactions to produce lower oxides of titanium, elemental titanium, and titanium carbide in accordance with the following chemical equations:

(1) $TiO_2+C \rightarrow TiO+CO$ (becomes favorable about 900–1000° C.)

(2) $TiO_2+2C \rightarrow Ti+2CO$ (becomes favorable about 1500–1600° C.)

(3) $TiO_2+CO \rightarrow TiO+CO_2$ (favorable above 100° C.)

(4) $TiO_2+3C \rightarrow TiC+2CO$ (becomes favorable about 900–1000° C.)

(5) $TiO+2TiC \rightarrow 3Ti+2CO$ (becomes favorable about 2000–2100° C.)

A mixed product of TiO and TiC may be obtained in furnace 14 by carrying out the reaction at a temperature of 900–1100° C. In presence of excess carbon, titanium carbide will be the favored product near 1000° C. at atmospheric pressure according to reaction 3. However, it is desired to make the maximum of metal and a minimum of carbide and lower oxides, hence the furnace must be heated to from 1500–2100° C. with the proper carbon ratio to promote reactions 2 and 5. The carbon monoxide and dioxide formed during reduction is driven off under suitable conditions through line 16.

Products of the furnace other than carbon monoxide and carbon dioxide are cooled to about 700° C. and are in the form of a fused agglomerate containing titanium, titanium carbide and titanium monoxide plus impurities such as small amounts of iron, chromium, vanadium and silicon. This material is ground or pulverized in pulverizer 18 for further handling.

The pulverized titanium-titanium monoxide mixture is then charged to reactor 20, which is operated under conditions to exclude oxygen, nitrogen and moisture. This reactor is preferably maintained at a temperature above about 1225° C. and at substantially atmospheric pressure. Under the conditions of elevated temperature and controlled atmosphere, the pulverized crude titanium mixture introduced to the reactor is subjected to the action of a higher metal bromide vapor (MX_h) entering through line 22 so that an exothermic reaction results. The reaction in reactor 20 is so exothermic in nature that only enough heat to start up is needed from an external source. The temperature within the reactor is controlled by the amount of halide vapor input through line 22.

We have found that any of the halides which readily combine with titanium may be used to form the halide vapor entering reactor 20 through line 22. Principally we have formed metallic titanium according to our process using bromine as the combined halogen present in the higher metallic halides (MX_h) and the lower metallic halide (MX_l).

For the purpose of general explanation, the metal and halide portions of all compounds illustrated in the drawing are represented by the symbols "M" and "X," respectively with *"h"* and *"l"* designating the higher and lower halide form, respectively.

The vapor in line 22 is principally a higher halide of titanium (MX_h) but in some cases may include equilibrium amounts of lower halides. The vaporous higher halide enters reactor 20 through the bottom and passes upwardly through the pulverized titanium mixture and upon reaction therewith forms a vaporous mixture of

lower and higher halides (MX_l and MX_h) which is free of carbon and impurities such as titanium monoxide, titanium dioxide and titanium carbide and which is removed from the top of reactor 20 through line 24. The maximum temperature which may be maintained in the reactor 20 must be below the decomposition temperature of the lower halide (MX_l).

The titanium higher halides function somewhat in the manner of carriers in accordance with specific reactions illustrated by the following equations:

(6) $Ti+2TiX_3 \rightarrow 3TiX_2$

(7) $Ti+TiX_4 \rightarrow 2TiX_2$

The titanium oxides and carbide present in the reactor charge that do not react with the higher halides under the aforementioned conditions, remain behind in the reactor as impurities. The carbon may be removed through line 26 and returned to pulverizer 12.

The impurities of line 28, comprising mainly titanium carbide and titanium monoxide, can be introduced into an auxiliary reactor (not shown) for further reaction to produce lower halides of titanium according to the following equations:

(8) $2TiO+3TiX_4 \rightarrow TiO+4TiX_3$

(9) $TiC+3TiX_4 \rightarrow C+4TiX_3$

Both of these reactions are favorable at temperatures below about 500° C.; hence such auxiliary reactor should be operated at about 400° C. while the tetrahalide vapor is introduced. This reactor should be operated batchwise so that after charging and reacting the solid titanium carbide and titanium monoxide with the tetrahalide vapor, such reactor is then heated to the melting point of the dihalide of titanium. Under these conditions, the trihalide disproportionates to dihalide and tetrahalide and the liquid dihalide may thereafter flow to reactor 30 to join the flow of liquid dihalide in line 24. The tetrahalide vapors may remain in the auxiliary reactor to react with a fresh charge of titanium carbide and titanium monoxide at the lower temperatures with additional tetrahalide added as required.

The vaporous lower and higher halide mixture (MX_l and MX_h) removed from reactor 20 through line 24 is then charged to a second reactor 30 which contains a plurality of electric heating elements generally indicated at 32. Each heating element is enclosed in a metal (M) sheath 34 and is maintained at a temperature of from 800° C. to 1500° C. The vaporous lower halide is condensed to form a liquid pool of the lower halide within reactor 30 which is maintained by the sheathed heaters to an average temperature of between 625° C. and 1225° C. and in this temperature range, the lower metallic halide is thermally disproportionated to form the metal, which deposits on the sheaths or collectors in a high state of purity, and to higher metallic halides (MX_h).

The decomposition of titanium dihalide to yield metallic titanium is according to the following equation:

(10) $2TiX_2 \longrightarrow Ti + TiX_4$ (liquid) (solid) (gas)

Any titanium trihalide which may be present is generally unstable and dissociates into titanium dihalide and titanium tetrahalide. The tetrahalide and some of the unreacted dihalide formed during the thermal disproportionation in reactor 30 is in a gaseous state and is removed through line 36 and pumped by pump 38 to condenser 40. In condenser 40, the gaseous mixture is cooled to a point whereby any titanium dihalide is condensed for return to reactor 30 in line 42 while the gaseous titanium tetrahalide is recirculated to line 22 through line 44 and provides substantially all of the tetrahalide requirement of reactor 20.

After the initial starting up of our process, the halide used for reacting with titanium proceeds in continuous circulation between reactors 20 and 30. Only a small

amount of the higher halide (MX_h) is necessary as make-up since the halide circuit is substantially closed with only small amounts of halide loss through the formation of volatile halides of the metallic impurities in the raw material.

Within the reactor **30** there is a continuous deposition and growth of metal on the heater sheaths **34** whereby they obtain the form of an ingot. Periodically the sheaths are removed and form the pure metal product, after which a new sheath is placed over the heating element and returned to the liquid pool of lower metallic halide.

Around each heater sheath is a refractory thermal barrier **46** which acts to substantially shield the liquid pool of lower halide from the higher temperature of the heater while at the same time directs the liquid halide in recirculating flow past the sheath for disproportionation.

In some instances the heating elements may also be maintained in the vapor phase over the liquid in reactor **30** as for example where it is found that the particular lower halide used disproportionates more rapidly as a vapor.

To illustrate a preferred embodiment of our process, operating conditions for the deposition of high purity titanium, are set forth in the following example.

Example

Vaporous titanium tetrabromide ($TiBr_4$) at a temperature in the neighborhood of 525° C. reacts rapidly with crushed slag (comprised of lower titanium oxides, titanium, titanium carbide and small amounts of impurities) in a bed maintained at a temperature in the neighborhood of 1375° C. at atmospheric pressure to form a vaporous mixture comprised of the lower and higher bromides of titanium. The dibromide is then condensed to form a liquid pool at a point removed from the slag bed. The liquid titanium dibromide, maintained at a temperature in the neighborhood of 750° C. at atmospheric pressure, disproportionates to titanium and titanium tetrabromide vapor in the presence of a heated titanium sheath (1050° C.) immersed within the pool. The titanium tetrabromide vapor is continuously withdrawn from the space above the pool and recirculated for use as the slag halogenating media. Analysis of the titanium coating on the titanium sheath shows only slight porosity and the presence of only trace impurities.

Having now described our invention with regard to the production of elemental titanium, zirconium, hafnium, tungsten and uranium and having given an example of a preferred embodiment of our process using titanium as the exemplified product, we desire a broad interpretation of the invention within the scope of the disclosure herein and the following claims.

We claim:

1. The method of producing a metal selected from the group consisting of titanium, zirconium, hafnium, tungsten and uranium by the disproportionation of a lower bromide of the metal to form the metal and a higher bromide of the metal which comprises: halogenating a crude mixture of said metal with a higher bromide of said metal to form a lower bromide of said metal; effecting said halogenation in a first reaction zone and at a temperature above the boiling point of said lower bromide of the metal and above the boiling point of said higher bromide of the metal thereby to form said lower bromide of said metal in said zone; withdrawing said lower bromide as a vapor from said first reaction zone; condensing said vaporous lower bromide and effecting the disproportionation of said condensed lower bromide in a second reaction zone in the presence of a heated body of said metal by forming a liquid pool consisting primarily of said lower bromide around said body while maintaining the liquid pool at a temperature above the melting point and below the boiling point of said lower bromide, said body being heated to a temperature sufficient to maintain said pool temperature; depositing a substantially solid layer of disproportionated metal on said body; and recirculating the higher bromide formed during disproportionation of said first reaction zone to provide the higher bromide utilized for said halogenation.

2. The method of producing a metal selected from the group consisting of titanium, zirconium, hafnium, tungsten and uranium by the disproportionation of a lower bromide of the metal to form the metal and a higher bromide of the metal which comprises: halogenating a crude mixture of said metal with a higher bromide of said metal to form a lower bromide of said metal; effecting said halogenation in a first reaction zone and at a temperature above the boiling point of said lower bromide of the metal and above the boiling point of said higher bromide of the metal thereby to form said lower bromide of said metal in said zone; withdrawing said lower bromide as a vapor from said first reaction zone; condensing said vaporous lower bromide and effecting the disproportionation of said condensed lower bromide in a second reaction zone in the presence of a heated body of said metal by forming a liquid pool consisting primarily of said lower bromide around said body while maintaining the liquid pool at a temperature above the melting point and below the boiling point of said lower bromide by thermally induced circulation of said liquid up through a shield surrounding said body and over said body, said body being heated to a temperature sufficient to maintain said pool temperature; depositing a substantially solid layer of disproportionated metal on said body; and recirculating the higher bromide formed during disproportionation to said first reaction zone to provide the higher bromide utilized for said halogenation.

3. The method of producing titanium by the disproportionation of a lower bromide of titanium to form titanium and a higher bromide of titanium which comprises: halogenating a crude mixture of titanium with a higher bromide of titanium to form a lower bromide of titanium, effecting said halogenation in a first reaction zone and at a temperature above the boiling point of said lower bromide of titanium and above the boiling point of said higher bromide of titanium thereby to form said lower bromide of titanium in said zone; withdrawing said lower bromide as a vapor from said first reaction zone; condensing said vaporous lower bromide and effecting the disproportionation of said condensed lower bromide in a second reaction zone in the presence of a heated body of titanium by forming a liquid pool consisting primarily of said lower bromide around said body while maintaining the liquid pool at a temperature above the melting point and below the boiling point of said lower bromide, said body being heated to a temperature sufficient to maintain said pool temperature; depositing a substantially solid layer of disproportionated titanium on said body; and recirculating the higher bromide formed during disproportionation to said first reaction zone to provide the higher bromide utilized for said halogenation.

4. The method of producing zirconium by the disproportionation of a lower bromide of zirconium to form zirconium and a higher bromide of zirconium which comprises: halogenating a crude mixture of zirconium with a higher bromide of zirconium to form a lower bromide of zirconium; effecting said halogenation in a first reaction zone and at a temperature above the boiling point of said lower bromide of zirconium and above the boiling point of said higher bromide of zirconium thereby to form said lower bromide of zirconium in said zone; withdrawing said lower bromide as a vapor from said first reaction zone; condensing said vaporous lower bromide and effecting the disproportionation of said condensed lower bromide in a second reaction zone in the presence of a heated body of zirconium by forming a liquid pool consisting primarily of said lower bromide around said body while maintaining the liquid pool at a temperature above the melting point and below the boil-

ing point of said lower bromide, said body being heated to a temperature sufficient to maintain said pool temperature; depositing a substantially solid layer of disproportionated zirconium on said body; and recirculating the higher bromide formed during disproportionation to said first reaction zone to provide the higher bromide utilized for said halogenation.

5. The method of producing hafnium by the disproportionation of a lower bromide of hafnium to form hafnium and a higher bromide of hafnium which comprises: halogenating a crude mixture of hafnium with a higher bromide of hafnium to form a lower bromide of hafnium; effecting said halogenation in a first reaction zone and at a temperature above the boiling point of said lower bromide of hafnium and above the boiling point of said higher bromide of hafnium thereby to form said lower bromide of hafnium in said zone; withdrawing said lower bromide as a vapor from said first reaction zone; condensing said vaporous lower bromide and effecting the disproportionation of said condensed lower bromide in a second reaction zone in the presence of a heated body of hafnium by forming a liquid pool consisting primarily of said lower bromide around said body while maintaining the liquid pool at a temperature above the melting point and below the boiling point of said lower bromide, said body being heated to a temperature sufficient to maintain said pool temperature; depositing a substantially solid layer of disproportionated hafnium on said body; and recirculating the higher bromide formed during disproportionation to said first reaction zone to provide the higher bromide utilized for said halogenation.

6. The method of producing tungsten by the disproportionation of a lower bromide of tungsten to form tungsten and a higher bromide of tungsten which comprises: halogenating a crude mixture of tungsten with a higher bromide of tungsten to form a lower bromide of tungsten; effecting said halogenation in a first reaction zone and at a temperature above the boiling point of said lower bromide of tungsten and above the boiling point of said higher bromide of tungsten thereby to form said lower bromide of tungsten in said zone; withdrawing said lower bromide as a vapor from said first reaction zone; condensing said vaporous lower bromide and effecting the disproportionation of said condensed lower bromide in a second reaction zone in the presence of a heated body of tungsten by forming a liquid pool consisting primarily of said lower bromide around said body while maintaining the liquid pool at a temperature above the melting point and below the boiling point of said lower bromide, said body being heated to a temperature sufficient to maintain said pool temperature; depositing a substantially solid layer of disproportionated tungsten on said body; and recirculating the higher bromide formed during disproportionation to said first reaction zone to provide the higher bromide utilized for said halogenation.

7. The method of producing uranium by the disproportionation of a lower bromide of uranium to form uranium and a higher bromide of uranium which comprises: halogenating a crude mixture of uranium with a higher bromide of uranium to form a lower bromide of uranium; effecting said halogenation in a first reaction zone and at a temperature above the boiling point of said lower bromide of uranium and above the boiling point of said higher bromide of uranium thereby to form said lower bromide of uranium in said zone; withdrawing said lower bromide as a vapor from said first reaction zone; condensing said vaporous lower bromide and effecting the disproportionation of said condensed lower bromide in a second reaction zone in the presence of a heated body of uranium by forming a liquid pool consisting primarily of said lower bromide around said body while maintaining the liquid pool at a temperature above the melting point and below the boiling point of said lower bromide, said body being heated to a temperature sufficient to maintain said pool temperature; depositing a substantially solid layer of disproportionated uranium on said body; and recirculating the higher bromide formed during disproportionation to said first reaction zone to provide the higher bromide utilized for said halogenation.

8. The method of producing a metal selected from the group consisting of titanium, zirconium, hafnium, tungsten and uranium by the disproportionation of a lower bromide of the metal to form the metal and a higher bromide of the metal which comprises: halogenating in a first reaction zone a crude mixture of said metal with a higher bromide of said metal to form a lower bromide of said metal and solid impurities including oxides and carbides of said metal; withdrawing said lower bromide as a vapor from said first reaction zone; condensing said vaporous lower bromide of said metal; separately halogenating in a second reaction zone said solid impurities with a second portion of said higher bromide of said metal to form a second source of the lower bromide of said metal; withdrawing said second portion of said lower bromide as a liquid from said second reaction zone; effecting in a third reaction zone the disproportionation of the combined portions of the liquid lower bromide of said metal in substantially solid layer form into said metal and the higher bromide of said metal; and recirculating said higher bromide of said metal as said halogenating media.

9. The method of producing relatively pure metals as claimed in claim 8 wherein the crude mixture is halogenated at a temperature above the boiling point of said lower bromide of said metal and the impurities from said first halogenation are separately halogenated at a temperature below the melting point of said lower bromide of said metal and above the boiling point of said higher bromide of said metal.

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