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**METHOD FOR PRODUCING EASILY OXIDIZED HIGH MELTING POINT METALS AND THEIR ALLOYS****Lucio F. Mondolfo, Chicago, Ill., assignor to The Illinois Institute of Technology, Chicago, Ill., a corporation of Illinois****No Drawing. Application January 13, 1955, Serial No. 481,705****10 Claims. (Cl. 75-63)**

This invention relates to methods of producing easily oxidized high melting point elements and alloys and to methods of recovering such metals from their alloys and oxides, and to the resulting products.

Prior art methods of recovering such metals have been expensive, have not yielded elements of the purity desired except with difficulty, and have suffered from other deficiencies.

Among the objects of the present invention is the production of such elements of high purity and low cost and at relatively low temperatures.

Further objects include the production of such elements in the form of alloys of two or more of such elements.

Still further objects include the production of such elements and their alloys by direct smelting of oxides.

Still further objects and advantages of the present invention will appear from the more detailed description given below, it being understood that such more detailed description is given by way of illustration and explanation only, and not by way of limitation, since various changes therein may be made by those skilled in the art without departing from the scope and spirit of the present invention.

In the present invention, oxides of elements or any of their nuclides, whose oxides have heats of formation lower than that of aluminum oxide are subjected to reduction at elevated temperatures with aluminum to form an aluminum alloy of such element, and the resulting aluminum alloy is subjected to leaching with magnesium or other metal that forms a low melting eutectic with aluminum, whereby said elements may be obtained in high degree of purity at low cost.

The elements recovered are desirably those having high melting points and which exhibit great reactivity with oxygen, nitrogen and carbon, and include titanium, niobium (columbium), hafnium, zirconium, boron, vanadium, chromium, manganese, etc. Alloys to be leached may be obtained from any source, but desirably they are the aluminum alloys formed in the initial stages of the complete process as by reacting the element or metal oxide with aluminum, since such aluminum alloys may be obtained in condition that enables them to be subjected directly to the leaching progress, thereby resulting in a direct continuous process for producing high purity elements or metals or their alloys with one another at relatively low cost. Also, in some cases, the aluminum alloys may be produced by ore smelting of the oxides of the high melting point element or metal with aluminum oxide.

In the steps of forming the aluminum alloys, the reaction may be carried out in any desired environment since the aluminum may be present in amount to blanket or protect the high melting point element or metal or any of their nuclides against oxidation, nitrification, etc.; or an inert atmosphere may be used.

In the first step the reaction may be carried out by bringing together the aluminum and the metal oxide at a

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temperature at which the reaction takes place within a reasonable time. To speed up the reaction it is preferable to have contact between aluminum and metal oxide as intimate as possible. For this reason the powdered metal or other elemental oxide may be premixed with aluminum powder and compacted, but this is not essential. Intimate contact may be obtained by stirring the metal oxide into the molten aluminum or by the use of fluxes that dissolve aluminum oxide or the metal oxide. A fluidized reaction mixture may be obtained in this or any other desired way.

The composition of the aluminum-metal alloy being prepared depends to some extent on the metal to be produced. Any composition ranging from 1 to 99% of the metal can be used, but it is preferable if the alloy produced has a relatively low melting point and if sufficient aluminum is present to insure protection of the metal. At the same time the aluminum content should not be too high because that increases the cost of the next step. For titanium the best results are obtained with alloys containing 20-30% titanium, although titanium can be collected from alloys containing as little as 1% and as high as 80%. For chromium, alloys in the range of 20-50% are the best.

As the reaction between aluminum and the metal oxide proceeds, aluminum oxide is formed. In most alloys this oxide tends to rise to the surface of the melt, from where it can be easily skimmed, its rise can also be accelerated by bubbling inert gases, such as helium or argon, through the melt, or any other gases inert under the conditions of treatment thus the gaseous halogens, e. g., fluorine, bromine and chlorine, may be used if the high melting point element or metal does not form a volatile halide at the temperature of operation.

The temperature in the reducing step may vary with the nature of the compounds present. It will generally be above about 2000° F. and below about 5000° F. But particular high melting point elements or metals may desirably be treated at temperatures that lie above certain minimums and below any temperature at which the operation becomes too violent for industrial operation. The most desirable minimum temperature for reduction of titanium dioxide is 2500° F. and will generally exceed that temperature; for chromium oxide it will be above about 2300° F; and for vanadium pentoxide the reaction proceeds slowly, between 2000 and 2400° F., becoming rapid at about 2500° F. Such reactions also depend on the relative amounts of the reactants and particularly their physical condition and intimacy of contact.

After the reduction, the products include an alloy of aluminum with the high melting point element or metal and aluminum oxide. Such products may be directly subjected to leaching but desirably any oxides present, being easily removed, are removed from the alloys.

The aluminum alloy of the high melting point element or metal is leached with magnesium or other element forming a low melting eutectic with aluminum.

For the leaching operation zinc, tin, mercury and their alloys, or other metals or alloys forming low melting eutectics with aluminum may be used. Magnesium, however, either pure or mixed with one or more of the above mentioned metals or alloys, is the preferred one because of the wide range of low melting alloys that it forms with aluminum and because of the low or negligible solubility of the high melting point metals in it. An inert atmosphere or environment is desirably employed when leaching with magnesium, but is not essential. Such atmosphere may be produced either by the use of helium or argon gas or by the use of the normal cover fluxes used during the melting of magnesium alloys.

The leaching step may be carried out at temperatures

and with concentrations at which the reaction mixture separates into two parts:

- (1) Molten aluminum-magnesium (or other additions) alloy.
- (2) Solid particles of the element or metal or alloy to be prepared.

Such products may then be separated by decantation, filtration, centrifuging or in any other desired way.

The removal of aluminum from the metal may be done in one step or preferably in several steps. In commercial practice a countercurrent flow of the magnesium and the alloy may be used to get the maximum leaching with the minimum amount of magnesium.

The amount of magnesium in contact with the alloy is not critical; it should desirably be at least  $\frac{1}{3}$  by weight of the aluminum present in the alloy and for best results should be increased as the amount of aluminum decreases; there is no upper limit to the amount of magnesium. The temperature at which the leaching is done is not very critical. Any temperature above the melting point but below the boiling point of the aluminum-magnesium composition may be used; however, the lower the temperature, the slower the diffusion of the aluminum out of the aluminum metal compounds into the molten magnesium; the higher the temperature, the faster the leaching, but the higher the amount of metal that dissolves into the magnesium. For best results, probably the leaching may be started at high temperature (up to 1100° C. for example) to insure rapid mixing, with subsequent cooling to about 460–500° C. for thereabouts to precipitate out the metal to be recovered.

The separation of the two products: molten aluminum-magnesium alloy and solid particles of metal in most cases may be done by decantation since the difference of density is very large. When zinc is used, centrifuging may be used to accelerate the separation since the density differences will be smaller. If the difference of density is too small for either decantation or centrifuging, filtration may be used to separate the solid particles from the liquid.

If during this separation some magnesium or other leaching reagent remains entrapped among the particles of solid metal, its removal can be achieved either by distillation (in the case of magnesium, zinc, tin or mercury) or by treating the metal particles with an acid or base which will dissolve the leaching agent but not the metal. When producing titanium, magnesium, zinc or tin can be removed by leaching with diluted hydrochloric acid; tin and zinc with diluted sodium hydroxide; and when producing chromium, magnesium or zinc can be removed with diluted nitric acid, and so on.

Among the advantages of the methods disclosed herein, the following may be noted:

(1) The metals may be produced from their oxides, which generally can be prepared of high purity at little cost. The method may also be used for the purification of secondary metal or of low purity metal produced by other methods. By alloying the impure metal with aluminum, its impurities such as oxides, carbides, nitrides may be separated out of the aluminum metal alloy.

(2) The method may be used to produce alloys containing two or more elements or metals. The mixing of the components of the alloys may be done at any stage of the process, from the mixing of the oxides to the mixing of the finished product.

(3) At least with some of the metals, such as manganese and chromium, it is possible to produce the aluminum-metal alloy starting from aluminum oxide and metal oxide, by arc smelting the oxides. In this way, not only the metal is produced, but also aluminum.

(4) The temperatures required for the process are relatively low, never exceeding 1200–1500° C., thus facilitating operations. Most of the time the metal to be produced is dispersed into aluminum or magnesium (or both) which will protect it from contamination; thus

elaborate arrangements to prevent contamination are not necessary.

The following examples will illustrate the invention, parts being by weight unless otherwise indicated.

#### A. Preparation of alloys

Alloys of titanium, chromium and vanadium were prepared from their respective oxides, using aluminum as a reducing agent. Compacts of oxides and aluminum powder (wt. ratio 1:1) were charged in molten aluminum. The reduction of titanium dioxide was carried out at temperature above 2500° F. Chromium pentoxide was reduced at temperature above 2300° F. The reduction of vanadium pentoxide took place very slowly between 2000 and 2400° F., but was very violent at 2500° F.

#### (1) AlTi alloys:

Alloy E	CHARGE			
	(Fig) Al	Compacts (1:1) TiO <sub>2</sub> -Al powder	Weight of Alloy in lbs.	Ti Content, wt. percent
71-A	3.75#	0.65#	3	5-10
71-D	3.75#	0.85#	3	10
72-A	2.25#	1.1#	2	15
72-B	3#	3#	1.5	25
87-A	1,500 gr.	750 gr.	2.5	10
87-B	1,500 gr.	700 gr.	2.5	10
87-C	1,110 gr.	1,000 gr.	2.0	16.01
87-D	1,080 gr.	750 gr.	2.5	12.2
90-A	310 gr.	200 gr.	0.5	10-15

#### (2) AlCr alloy:

4# of Al

1.75# of compact (Cr<sub>2</sub>O<sub>3</sub>=Al, 1:1)

Wt. of AlCr alloy=3# containing about 10% Cr

#### (3) 4# of Al

1.5# of compact (V<sub>2</sub>O<sub>5</sub>=Al, 1:1)

Wt. of AlV alloy=3# containing about 10% V

#### B. Leaching of the alloys with magnesium

#### (1) Under argon atmosphere:

Leaching of AlTi alloy:

(a) 200 gr. of AlTi alloy (Ti=10%)

570 gr. of Mg

Number of leach=3 or 3.75# of Mg

Wt. of residue (Mg leached out with dilute HCl)=15 gr.

Chemical composition of residue, Al=18.81%

(b) 160 gr. of AlTi alloy (Ti=10%)

1200 gr. of Mg

Number of leach=1 (20 hrs. at 1800° F. and severe gas flushing)

Wt. of residue (HCl leach)=10 gr.

Chemical composition, Al=14.58

#### (2) Under flux cover (flux was Dow Chemical #230):

Leaching of AlTi alloy:

(a) 625 gr. of AlTi alloy (Ti=10%)

750 gr. of Mg

Number of leach=10 or 17# of Mg

Wt. of distillation and residue=45 gr.

Chemical composition, Al=55.5%

(b) 425 gr. of AlTi alloy (Ti=10%)

750 gr. of Mg

Number of leach=17 or 27# of Mg

Wt. of distillation residue=30 gr.

Chemical composition of residue, Al=12.77%

Leaching of AlCr alloy:

(c) 300 gr. of AlCr alloy containing about 10% Cr

750 gr. of Mg

Number of leach=7 or 5.5# of Mg

Wt. of distillation residue=15 gr.

Chemical composition of residue, Al=22.37%

The nominal composition of Flux Dow Chemical No. 230 is:

55% KCl  
34% MgCl<sub>2</sub>  
9% BaCl<sub>2</sub>  
2% CaF<sub>2</sub>

In the examples given above, such terms as "Number of leach=3 or 3.75# of Mg" means: leached three times, each time with 570 gr. of Mg, thus using a total of 3.75 lbs. of Mg for the leaching. Other similar terms will be analogous in meaning.

Having thus set forth my invention, I claim:

1. The method for production of highly pure titanium which consists essentially in reducing titanium oxide with aluminum in the presence of molten aluminum in amount to protect the titanium formed, at a temperature of from about 2000° F. to 5000° F., in proportions of reactants to give an aluminum titanium alloy having an excess of aluminum thereby to protect the titanium, and leaching the resulting aluminum titanium alloy with a leaching agent selected from the group consisting of magnesium and its alloys, magnesium in amount at least one third of the amount of aluminum present in the aluminum-titanium alloy, at a temperature above the melting point of aluminum-magnesium alloy formed but below its boiling point, and separating the leach reaction mixture into two phases, one phase containing aluminum magnesium alloy substantially free of titanium and the other phase consisting essentially of titanium selected from the group consisting of pure titanium and alloys thereof.

2. The method of claim 1 in which the aluminum-titanium alloy contains from about 5% to 30% of titanium.

3. The method of claim 1 in which the leaching step is carried out with magnesium as the leaching agent at a temperature not exceeding about 932° F. in the latter portion of the leaching step.

4. The method of claim 1 in which the leaching step is carried out with a magnesium-zinc alloy.

5. The method of claim 1 in which the titanium oxide and aluminum are premixed and compressed prior to reduction.

6. The method of claim 1 in which the leaching step is started at temperature up to about 2012° F. and subsequently lowered to about 932° F.

7. The method for production of highly pure metals which consists essentially in reducing an oxide of a high melting point metal selected from the group consisting of titanium, niobium, hafnium, zirconium, boron, vanadium, chromium and manganese with aluminum in the presence of molten aluminum in amount to protect the high melting point metal formed, at a temperature of from about 2000° to 5000° in proportions to give an aluminum high melting point metal alloy having an excess of aluminum thereby to protect the high melting point metal, and leaching the resulting aluminum high melting point metal alloy with a magnesium leaching agent selected from the group consisting of magnesium and its alloys, the amount of leaching agent being at least one third of the amount of aluminum present in the aluminum high melting point metal alloy, at a temperature above the melting point of aluminum magnesium alloy formed but below its boiling point, and separating the leach reaction mixture into two phases, one phase containing aluminum-magnesium alloy substantially free of said high melting point metal and the other phase consisting essentially of said high melting point metal selected from the group consisting of said pure high melting point metal and its alloys.

8. The method of claim 7 in which the high melting point metal is titanium and the leaching metal is magnesium.

9. The method of claim 7 in which the high melting point metal is chromium and the leaching metal is magnesium.

10. The method of claim 7 in which the high melting point metal is vanadium and the leaching metal is magnesium.

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