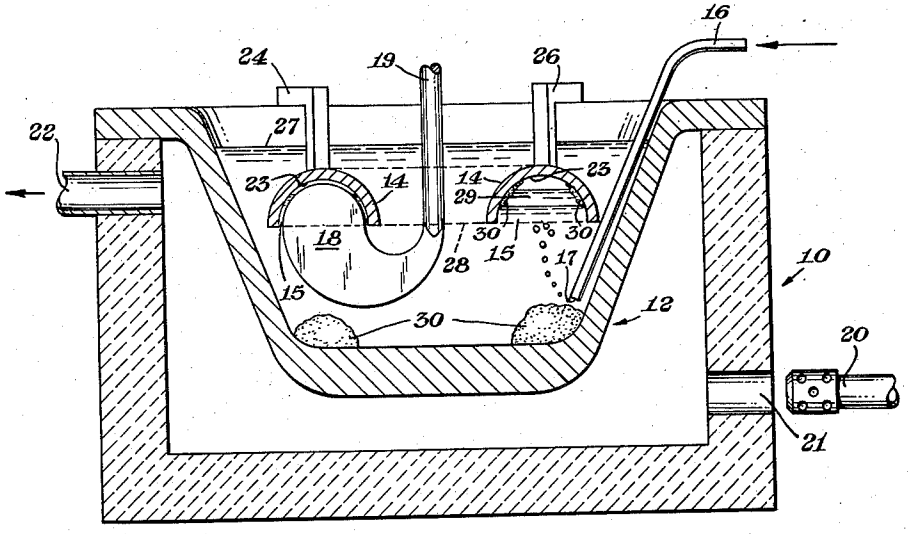
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METHOD OF PRODUCING CRUDE METAL

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INVENTOR.
Douglas S. Chisholm
BY
Griswold & Burdick
ATTORNEYS

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METHOD OF PRODUCING CRUDE METAL

Douglas S. Chisholm, Midland, Mich., assignor to The Dow Chemical Company, Midland, Mich., a corporation of Delaware

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The invention concerns the production of crude metals which are reducible from compounds containing them by the action of magnesium metal thereon. It more particularly concerns the reduction of a subgroup IVa metal halide to produce a subgroup IVa metal in a crude state suitable for further refining by electrolysis in a fused salt bath.

Methods of producing subgroup IVa metals, viz., titanium, hafnium, zirconium, and thorium in a sufficiently pure state for alloying and fabricating, are known. However, known methods are costly due to the highly reactive nature of subgroup IVa metals, thereby making such metals uneconomical for a number of uses for which their special properties make them highly desirable.

Methods of producing a refined subgroup IVa metal by electrolysis of crude metal are known. Among such methods is the method of producing refined titanium from crude titanium feed described in the United States Bureau of Mines, Report of Investigations, Number 5315 (February 1957). The method therein described employs an electrolytic cell for producing refined titanium from off-grade sponge and scrap containing appreciable percentages of titanium. Such a cell as therein described illustrates the type of electrolytic cell for which crude feed in the form of sponge and scrap containing not over about 9 to 10 percent contaminants is usable to produce a metal of satisfactory purity for general use. The Brinell hardness number of titanium, for example, was reduced from 314 to 78 by being electrorefined or electropurified in the cell described in said Bureau of Mines Report.

The method of employing the cell described in the aforesaid report consists chiefly of passing D.C. through a fused salt electrolyte which has immersed therein a conducting cathode and a crude titanium anode, under an inert gas atmosphere, wherein the crude titanium anode is gradually consumed by the ensuing electrolytic action, refined titanium collecting at the cathode and the impurities collecting as a sludge at the bottom of the electrolyte chamber.

Crude subgroup IVa metals of a purity of 89 to 91 percent are quite satisfactory for further refining in electrolytic cells generally and particularly in the cell described above. Methods of preparing crude feed for use in this type of cell have not heretofore been economically satisfactory, either because the preparatory process was too costly or the titanium feed was purer than that necessary or it was not pure enough for subsequent economical refinement in the electrolytic cell. Particularly noteworthy of a method not proving satisfactory for the production of such crude subgroup IVa metal, because the crude metal is not sufficiently pure, is that comprising the reduction of an ore containing an oxide thereof by heating it with carbon.

A desideratum then exists in the art of producing subgroup IVa metals and other metals having halides reducible by the interaction therewith of magnesium for an economical method of producing a crude feed containing such a metal suitable for refining in an electrolytic cell.

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The principal object of the invention, therefore, is to provide an apparatus for and a method of producing metals, particularly subgroup IVa metals, having a halide reducible by the interaction thereof with magnesium, which are useful as feed in an electrorefining cell. A more specific object is to provide a method of producing crude titanium metal for use as feed in the electrorefining cell of the type described in the United States Bureau of Mines Report of Investigation, Number 5315.

The method by which these and related objects of the invention are attained is made clear in the following description with reference to the annexed drawing and is particularly defined in the appended claims.

The invention is a method of preparing crude metals, especially subgroup IVa metals, having a halide reducible by magnesium metal to produce thereby suitable feed for refining in an electrolytic cell. The method consists essentially of superimposing molten magnesium on a molten saline flux of a greater density than the molten magnesium, passing a halide of the metal (to be produced) as a gas up through the molten flux into the molten magnesium thereby producing a sludge which contains the metal to be produced, removing the sludge thus produced from the flux, and thereafter leaching it to recover therefrom the crude metal, e.g., a subgroup IVa metal, which contains not over 9 to 11 percent impurities.

The drawing is a sectional elevation of an apparatus useful in practicing the method of the invention.

The production of titanium will be described for the purposes of illustrating the practice of the invention, but the practice of the invention is not limited thereto. Other metals having a halide reducible by the action of magnesium thereon fall within the scope of the invention.

In carrying out the invention, a saline flux of greater density than molten magnesium is placed in a suitable pot and melted. Magnesium metal is placed thereon and also melted, magnesium then forming a superimposing layer on top of the flux. A titanium halide which is volatile at the temperature of the flux is passed up through the flux into the molten magnesium as a gas according to the United States Patent 2,779,672. The halide may be admitted as a liquid or solid so long as it volatilizes upon contact with the molten flux. Unlike the method described in said patent, however, which has for its purpose the purification of magnesium, the method of the instant invention requires that the titanium halide, preferably $TiCl_4$, be passed up through the flux and into the molten magnesium beyond the time required for purification of the magnesium metal for a period of time sufficiently long for the $TiCl_4$ to fully react with the magnesium metal to form Ti metal and $MgCl_2$. Sludge forms and settles to the bottom of the flux, forming the intermediate product of the invention, from which crude titanium metal is thereafter produced by leaching said sludge to produce crude Ti metal useful in producing titanium metal of high purity by electrolysis in an electrorefining cell. The sludge continues to be formed so long as the halide, e.g., $TiCl_4$ is passed into the magnesium metal thus superimposed on the flux. Magnesium halide, e.g., $MgCl_2$, is formed as a by-product in the sludge thereby consuming

magnesium metal in the process. As a result thereof, magnesium metal must be added at intervals to the reaction vessel. The sludge may be removed by manual operation, as by scooping or dipping it out, or it may be continuously removed by an auger, a conveyor arrangement, or by other suitable mechanical handling means.

The sludge thus removed contains at least about 60 percent and usually at least 65 percent titanium and usually between about 28 and 32 percent water-soluble contaminants. After removal, the sludge is preferably comminuted. Thereafter, it is leached, preferably with an aqueous acid solution, e.g., a 1 to 10 percent and preferably about a 5 percent by weight aqueous HCl, until the impurities do not exceed about 11 percent. It is then ready for use as raw feed for further refining in an electrorefining or purification cell.

A preferred mode of practicing the invention is to employ the apparatus of the invention shown in the drawing. The drawing shows an apparatus comprising a gas-fired furnace setting **10**, cast steel melting pot **12** supported therein, removable hollow torus **14** having a downwardly extending open face **15** positioned substantially horizontally in pot **12** intermediate its top and bottom, titanium halide feed duct **16**, extending into the pot with open end **17** below torus face **15**, and scraper **18** which is rotatable by means of arm **19** which extends downwardly through the axis of **18** substantially centrally of torus **14**. Scraper blade **18** is shaped so that its upper edge matches the transverse section of underside **23** of torus **14**. Gas burner **20** at opening **21** and gas outlet **22** provide a means for heating pot **12** and for venting combustion gases, respectively. Torus **14** is supported by brackets **24** and **26**. Arm **19** of scraper **18** may be turned manually or can be turned by a train of gears, a belt, or the like attached to a source of mechanical power (not shown).

The following example illustrates the practice of the invention employing an apparatus of the type shown in the drawing. $MgCl_2$ was placed in melting pot **12** and melted by raising the temperature above its melting point by burning gas introduced at opening **21** in furnace setting **10**. The level of the melting $MgCl_2$ is above the torus as shown at **27**. Downwardly opening hollow torus **14** was then placed in the molten $MgCl_2$ at level **28**. Magnesium metal pieces in the form of about 1 pound ingots were then placed in the $MgCl_2$ below the open face of torus **14** by means of tongs and there released, whereupon they rose to the surface of the $MgCl_2$ in the aforesaid hollow cavity in torus **14** thereafter floating on the surface of the $MgCl_2$ as item **29** in the toroidal cavity displacing sufficient $MgCl_2$ to accommodate the Mg metal pieces, whereupon they melted. Trapped air in the cavity was substantially also displaced at this time; any remaining air reacted with magnesium metal and/or titanium and became an impurity in the sludge being formed. $TiCl_4$ was introduced as a liquid through tube **16**. The $TiCl_4$ gasified in tube **16** and entered the $MgCl_2$ flux as a gas and thereupon bubbled up to underside **23** of torus **14**. The rate of feed of $TiCl_4$ was regulated so that substantially all of it reacted with the magnesium metal confined within torus **14**. The reaction with the magnesium built up a loosely adherent sponge on underside **23** of the torus necessitating periodic removal by turning arm **19** so as to activate scraper **18**. The sludge thus loosened fell to the bottom of the pot, as represented by item **30** of the drawing, from whence it was periodically removed by ladling it out. The thus-removed sludge was then cast into molds.

When the titanium in the molds was cooled, it was removed, crushed and placed in a drum provided with an agitator and containing water which had been acidified with HCl to a 2 percent by weight solution. The sludge was then washed under agitation in the HCl solution. Water-soluble impurities were thereby removed. After twenty-four hours, the crude titanium was removed, water-rinsed and dried. The crude titanium thus produced according to the method of the invention contained 90.2 percent titanium. This is a satisfactory feed to employ in an electrolytic cell of the type described in the Bureau of Mines electropurification cell described hereinabove.

Advantages flowing from the invention are shown by the example which economically produced crude titanium feed without the need for inert gas or provision of elaborate measures to prevent contamination. The crude titanium is fully satisfactory for further refining to a low Brinell hardness, high-purity titanium in an electrolytic cell.

Having described the invention, what is claimed and desired to be protected by the Letters Patent is:

1. The method of producing a crude metal having a tetrahalide reducible by molten magnesium metal which comprises positioning a hollow torus, having an open face directed downward, below the level of a body of molten salt of greater density than molten magnesium selected from the class consisting of an alkali metal halide, an alkaline earth halide, and a mixture thereof; introducing pieces of magnesium metal into the molten salt below the open face of said torus; melting the magnesium metal and displacing molten salt from the torus thereby forming a contacting surface with said molten salt therebelow; introducing a gaseous tetrahalide of the metal to be produced in an amount sufficient to react with substantially all the molten magnesium metal; allowing the tetrahalide to contact the molten magnesium metal in said torus at a point directly below the open face of the torus to effect a reduction of the tetrahalide by the magnesium metal to yield a reaction product containing metal reduced from the halide, at least a portion of which adheres to the arcuate inner walls of the torus; removing such adhering reaction product by a revolving scraper means and causing the reaction product to accumulate in the lower part of the molten salt; removing the reaction product from the salt; and thereafter subjecting the thus removed reaction product to the leaching action of an aqueous solution containing at least one percent by weight of HCl.

2. The method of producing a crude metal having a tetrahalide reducible by molten magnesium metal which comprises: suspending solid pieces of magnesium metal within a confining means below the level of a molten salt bath having a greater density than the molten magnesium metal and being maintained at a temperature above the melting point of magnesium metal, thereby creating a reaction zone which is closed to communication upwardly and open to communication downwardly so that the magnesium metal displaces molten salt from said reaction zone and forms, when melted, a contacting surface with said molten salt therebelow; confining the molten magnesium metal in said reaction zone suspended in said molten salt bath; continuously admitting a tetrahalide of the metal to be produced, in the gaseous state, into the salt bath at a point substantially directly below the thus confined molten magnesium metal in an amount sufficient to effect a reaction with a substantial proportion of the molten magnesium metal in the reaction zone; allowing the tetrahalide to contact the molten magnesium metal in said reaction zone to produce a sludge having a density greater than the molten salt and containing the metal reduced from the tetrahalide; collecting the sludge thus produced in the lower part of the molten salt bath; removing the sludge from the bath; and leaching the so removed sludge with an aqueous solution of a mineral acid.

3. The method of claim 2 wherein the said tetrahalide is $TiCl_4$.

4. The method of claim 2 wherein said tetrahalide is $ZrCl_4$.

5. The method of claim 2 wherein the sludge is leached until it contains no more than 11 percent impurities.

6. The method of claim 2 wherein the leached sludge is subsequently water-washed and dried to provide crude feed metal for electro-refining.

7. The method of claim 2 wherein the salt bath consists essentially of $MgCl_2$.

8. The method of claim 2 wherein the aqueous solution of a mineral acid is 1 to 10 percent HCl by weight.

9. The method of claim 2 wherein the cross-section of said zone is an inverted U-shape and the lineal dimension describes an annulus positioned near the surface of said bath intermediate the center and sides thereof.

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