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METHOD OF PRODUCING REFRACTORY METAL

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This invention relates to the preparation of refractory metals such as titanium, zirconium, and the like, and particularly to an improved process for the preparation of such metals in which oxide contamination is minimized.

Procedures for the production of refractory metals such as titanium, zirconium, and the like, by the reduction of a halide of the desired metal with a reducing metal are well known. Illustrative of such processes are those disclosed in U.S. Patents Nos. 2,205,854, 2,556,763, 2,586,134, 2,621,121, 2,773,760 and others. Typical is the process for the reduction of titanium tetrachloride by magnesium metal in which a reaction vessel is charged with magnesium metal and heated under an inert atmosphere to above the melting point of magnesium. Titanium tetrachloride is then admitted to the vessel where it vaporizes and reacts with the molten magnesium to form titanium sponge. Although the commercial magnesium used for these reduction operations is carefully processed during its preparation, oxygen impurity in the form of magnesium oxide is normally present to the extent of about 0.01–0.04 weight percent and is transferred to the titanium sponge during the reduction operation. The presence of this oxygen impurity contributes materially to the quality degradation of the sponge because of the hardening effect of this deleterious impurity on the titanium metal.

The quite rigorous steps which are usually undertaken to clean the surface of the magnesium bars prior to use in these reactions is described in Bureau of Mines R.I. 4879, "Recent Practices at the Bureau of Mines, Boulder City, Nevada, Titanium Plant," by H. C. Fuller et al., page six. We have found that neither acid pickling nor the laborious hand scraping which is resorted to will produce an oxygen-free reagent. Apparently, the oxidation at the surface of the magnesium occurs rapidly even at room temperature and in contact with the normal atmosphere. This finding made it evident that the final cleaning of the magnesium should be done in some manner which would not permit air to contact the cleaned metal. Carrying out the whole operation in an atmosphere of inert argon would perhaps provide some improvement, but to do this on a commercial scale where a ton or more of magnesium metal must be cleaned and transferred into a reaction vessel would obviously entail a very costly, undesired operation. The desired purity might possibly be achieved by piping liquid, salt-purified magnesium held in air-free containers directly into the reaction vessel. This, however, is a very difficult transfer operation at the necessary temperature and would require much additional equipment. Furthermore, unless expensive metals or alloys are used, the molten magnesium will dissolve iron from the containers and undesired, additional contamination will ensue.

An object of this invention is to improve the quality of refractory metal products obtained from the reduction of a metal halide, and to provide substantially oxygen-free magnesium as a reducing metal to the reaction zone for reducing a refractory metal halide to its metal. A further object is to accomplish this in a commercially feasible manner. A specific object is to provide novel and effective means for employing commercially pure magnesium bars in a metal halide, especially a metal chloride reduction process while avoiding contamination of the product metal with normally accompanying oxygen impurities and without recourse to expensive cleaning steps under inert gas envelopes. A still further object is to improve the purity and quality of refractory metals such as titanium obtained in accordance with commercial methods. Other objects and advantages will be apparent from the following description of our invention.

The above and other objects are accomplished by this invention which broadly comprises contacting solid oxygen-carrying magnesium prior to its employment as a reducing metal in a reduction process, with freshly distilled, substantially oxygen-free magnesium chloride in a dry, air-free reaction chamber, melting the magnesium and the magnesium chloride to form a two-liquid system in said chamber, providing sufficient contact between the two liquid phases formed to permit the oxygen present in said magnesium to transfer to the magnesium chloride salt phase, removing the resulting oxygen-containing magnesium chloride phase from said chamber, and then reacting at an elevated temperature and under an inert atmosphere, the purified oxygen-free magnesium with a halide, particularly a chloride of a refractory metal such as titanium, zirconium, etc., to produce an improved, pure form of refractory metal.

The use of freshly distilled $MgCl_2$ and removal of oxygen-containing $MgCl_2$ from the reaction chamber prior to undertaking the reduction reaction are critical in this process. By the term "freshly distilled $MgCl_2$" is meant the salt that is vaporized, condensed, and used as the fluxing agent in the reaction chamber without contact with air and moisture. The preferred method of accomplishing this is to vaporize $MgCl_2$ in vacuum and condense the vapors on cooled solid magnesium metal present in the vessel in which the ensuring reduction reaction between the purified magnesium and a refractory metal chloride is to be carried out. While, for example, the distilled salt could be condensed as a liquid and conveyed to the reactor in molten state, the difficulties attending this high temperature handling render such an operation less preferable.

As a preferred cyclic method of operating our process, at least a portion of magnesium chloride by-product from a previous reduction can be used as the fluxing or purifying agent in the subsequent process step. In accordance therewith, titanium sponge obtained from a previous reduction reaction is purified by vacuum distilling its by-product magnesium chloride content into an associated, cooled receiver vessel containing magnesium bars and wherein the vapors condense on the bars and vessel wall. An inert atmosphere (argon, helium, krypton) is then maintained in the associated vessel, to let down the vacuum, the magnesium-magnesium chloride system melted and the molten magnesium chloride collected at the bottom of the vessel along with the magnesium oxide impurity removed from the magnesium. This salt layer is then removed prior to the introduction of the metal chloride (titanium or zirconium tetrachloride) reactant into the purified magnesium-containing vessel for reduction to the titanium or zirconium metal of exceptionally low oxygen content.

As noted, air is excluded during the purification and reduction stages of the process by means of an inert gas atmosphere maintenance, and such inert atmosphere is maintained in the chamber during the reaction and the inert gas is used for purging and letting down the vacuum after distillation. Every possible effort is made to prevent air leakage during the evacuated periods.

Contact between the fresh magnesium chloride distillate and magnesium to facilitate removal of the oxygen by the salt can be increased if desired by bubbling argon or other inert gas up through the molten system prior to separating the salt. This is not always necessary since certain procedures herein described will provide adequate contact without actual agitation.

The improvement of this invention is most effective when applied to the specific metal reduction process disclosed in U.S. 2,773,760. In that process, a plurality of similar reaction vessels are employed in a cyclic manner, with air absence in the systems being assured through use of argon and vacuum. In one vessel, reduction of, for example, $TiCl_4$ is effected with magnesium. The magnesium bars are placed in such vessel, it is then argon purged, and the bars melted. Titanium tetrachloride is then admitted to react with the magnesium at temperatures ranging from about 750–1100° C. and preferably between about 800° C. and 950° C. The by-product magnesium chloride is usually drained from the bottom of the vessel during or after the reaction. Residual $MgCl_2$ always remains, however, which, along with small amounts of magnesium and/or lower chlorides of titanium, are vacuum distilled into an associated second vessel in communication with the first vessel by means of a suitably heated cross-over valve-controlled conduit during argon purging. Prior to effecting such communication or connection between the vessels, the second vessel is loaded with magnesium in ingot, bar or other form. Preferably, a bar form of product is employed with the bars cross-piled to provide a maximum arrangement of surfaces for condensation of the salt vapors. After placing the vessels in direct communication with each other, the system is evacuated and distillation accomplished in the usual manner by heating the first vessel and cross-over or communicating conduit while the second or condensing vessel is subjected to desired cooling by an encircling blast of air thereover. Upon completion of the distillation, the vacuum is let down with argon, the cross-over pipe disconnected and blanked off under an argon purge and the batch of refractory metal product is recovered from the first vessel. The second vessel, meanwhile, is placed in a furnace and heated to about 725–1000° C. to melt the magnesium and the condensed magnesium chloride. At this critical point, the improvement of the present invention is applied by draining and removing from the vessel the molten $MgCl_2$ which has settled down to its bottom under the pool of liquid Mg. As a result, the undesired oxide content of the magnesium becomes transferred to the salt phase and is removed from the system. The purified molten Mg remaining is then reacted with $TiCl_4$ immediately in the same vessel under an inert atmosphere at the temperatures above mentioned and before any air or moisture admission occurs, to obtain substantially pure titanium metal of exceptionally low oxygen content.

To a clearer understanding of the invention, the following example is given. This is merely illustrative and is not to be considered as limiting the scope of the invention.

Example

The reaction vessels used were about 4 ft. I.D. by 10 ft. deep, made of alloy steel capable of being heated in air to at least 1000° C. and were lined with thin sheet iron or mild steel to prevent destructive action of the molten magnesium on the alloy steel vessels. The liner used continued as an outlet pipe through the bottom of the vessel, said outlet means being connected to a valve for controlling the salt draining operation. The vessels were provided with a flanged cover, fitted and sealed by O rings to make a vacuum-tight assembly, with inlets associated with the cover for $TiCl_4$ introduction and purging argon, as well as with connections for a heated, 8-inch diameter cross-over pipe. Suitable thermocouple attachments were provided at the reactor walls, in the covered and in the cross-over pipe. Each vessel was set in a conventional furnace adapted to heat the vessel to any desired temperature, and provided with means for admitting circulating cooling air. The two reactors were set in adjacent locations where one could be heated, while the other was cooled to accomplish the distillation desired. The vacuum line was connected to the bottom outlet of the cooled vessel for distillation. A cyclic process was carried out as follows: A hot reaction vessel, containing the products of a previous reduction and draining operation including about 350 lbs. of $MgCl_2$ was located in a furnace well. A second associated reaction vessel was loaded with 3300 lbs. of magnesium bars taken from storage in a normal clean condition without further surface cleaning. The vessel was then covered, moved to a station adjacent the first vessel, and purged with argon. During its final purging, the intercommunicating cross-over pipe connection was made without admitting air to the system, and thereafter the system was evacuated to about 50 microns of mercury, with the second vessel being cooled by circulating air. The temperature in the first vessel was then gradually raised to about 950° C. and held at that temperature for 5 hours. At this time, the pressure in the retort vessel decreased rather quickly to about 40 microns to indicate that $MgCl_2$ distillation was about completed. The temperature of the first vessel was then raised to about 1000° C. and maintained at that temperature for about one hour and then cooled and the vacuum let down with argon. The connecting cross-over conduit was removed and the vessel openings blanked off under argon purging. The second vessel containing the Mg bars and the distillate was then moved to a reduction station, placed in the furnace and a connection made to the $TiCl_4$ supply. Both a flow meter and a weigh tank were used to control the addition of $TiCl_4$. The vessel was heated to about 825° C. to melt the Mg and then the $MgCl_2$. After about 2 hours at 800–825° C., the settled liquid $MgCl_2$ was drained from the bottom of the vessel into a drum, the draining operation being stopped when traces of metallic Mg appeared at the tap-hole. The drained salt weighed 345 lbs. $TiCl_4$ was then fed to the top of the reactor and combined control of feed rate, furnace heating and cooling was employed to maintain the temperature of the reaction mass between about 850° C. and 950° C. as determined by thermocouples suitably placed along the walls and cover of the vessel. When 13,100 lbs. or about 90% of the theoretically required $TiCl_4$ had been added, taking into account the fact that most of the excess Mg from the previous reduction had distilled over with the $MgCl_2$, the $TiCl_4$ feed was stopped and the mass held between 950° C. and 975° C. for 2 hours. All but about 350 pounds of the by-product salt was then drained out and the distillation phase of the cycle was then set up. The cross-over pipe connection was made to a third reaction vessel containing magnesium bars and the system evacuated as before and the process repeated. Upon completion of the distillation, the titanium product in the second vessel was recovered and sampled. This product upon being compared with other titanium products similarly prepared but without recourse to the critical salt extraction and draining steps of this invention exhibited the following characteristics:

	B.H.N.[1]	Oxygen, p.p.m.
1. Product of above Example	97	570
2. Prior art titanium product using same lot of Mg bars in same condition, but without draining the $MgCl_2$ distillate	115	940
3. Prior art titanium product using same Mg bars carefully precleaned by acid pickle and drying but no $MgCl_2$ distillate draining	113	880

[1] Brinell Hardness Number by method described in the 1955 Book of Standards of the American Society for Testing Materials under ASTM designation E 10-54T.

As will be evident, the particular conditions encountered in salt purifying the magnesium by the process of this invention are uniquely suited to the manufacture of our improved high purity titanium product. The invention is obviously applicable to the production of other

Fourth Group metals, especially zirconium, through reduction of their chlorides. The purification step is carried out in situ, that is, in the vessel where the purification and reduction reaction is to be carried out, with no need to transfer the magnesium or bring it into contact with air. Furthermore, recourse to our preferred detailed procedure will be found to provide a desired, intimate contact between the magnesium and the magnesium chloride, with this contact being most intimate at the exact location of the oxide impurity. The highly effective results which we achieve are believed to be due, first, to the fact that the freshly distilled magnesium chloride, evaporating from the titanium sponge, is as free of oxygen as is conceivably possible, and its capacity to absorb all traces of oxide from the magnesium is at a desired maximum. Secondly, since the magnesium bars are kept cold, the $MgCl_2$ condensation in solid form over their surfaces and in contact with the oxide surface impurity is advantageously promoted. At the end of the distillation, the salt-coated bars are heated, rather gradually due to the size of the vessel and the poor heat transfer across the gas spaces, to the desired melting temperature, say, from about 725–1000° C. The magnesium melts first, flowing to the bottom of the vessel to leave a skeleton or shell of solid $MgCl_2$ which probably retains most of the oxide resdiue. As the temperature increases, the salt melts and flows over the surface of the molten magnesium and, being heavier, sinks through it. The oxide dissolves in the molten $MgCl_2$ and in consequence of this thorough contact between the salt and magnesium, a high degree of purification results. The impure magnesium chloride is then easily removed from the reaction zone by draining and prior to initiating the refractory metal chloride reduction.

While we preferably employ freshly distilled $MgCl_2$ from a previous batch of refractory metal in a cyclic operation as the purest obtainable, commercial dry $MgCl_2$ can be used and placed in a suitable retort and distilled onto the magnesium charge. This procedure would be useful in starting a cyclic operation and would improve the purity of the product of the first cycle.

The procedures of this invention are flexible in that the amount of freshly distilled magnesium chloride may be varied. In the example, the weight of the distilled $MgCl_2$ is about 10% of the weight of the Mg to be purified. This is about the practical minimum since about this proportion is retained by the titanium sponge after full draining. By controlled draining, considerably more $MgCl_2$ may be left for distillation, if desired. Increasing the amount of $MgCl_2$ distilled to, say, 25% of the weight of the Mg will assure more complete purification and also give greater opportunity for removing any soluble oxides from the interior surfaces of the reactor.

The advantage obtained by using the particular sequence of critical steps of this invention is clearly shown in the decreased oxygen content of the product of the example as compared with prior art products. This is particularly evident in view of the fact that all the magnesium used had been purified by prior art molten salt fluxing methods before being cast into the commercial bars.

This application is a continuation-in-part of our copending application Serial No. 771,716, filed November 4, 1958, now abandoned.

We claim:

1. A process for preparing a Fourth Group refractory metal which comprises contacting solid, oxygen-containing magnesium having about a 0.01 to 0.04 weight percent oxygen content with vaporized, substantially oxygen-free magnesium chloride within a closed, dry, air-free reaction chamber, condensing said vaporized magnesium chloride on the surface of said solid magnesium within said chamber, melting said magnesium and magnesium chloride in said chamber under temperatures ranging from 725–1000° C., and contacting the two resulting liquid phases therein to permit oxygen present in said magnesium to transfer to said magnesium chloride, removing from said chamber the resulting oxygen-containing magnesium chloride, and then reacting the purified oxygen-free magnesium which remains in said chamber with a chloride of a Fourth Group refractory metal, effecting said reaction at a temperature ranging from 750–1100° C. under an inert atmosphere and prior to admitting air into said chamber, and recovering the resulting pure refractory metal product.

2. A process for preparing a Fourth Group refractory metal which comprises condensing vaporized, substantially oxygen-free magnesium chloride on the surface of solid, oxygen-carrying magnesium having about a 0.01 to 0.04 weight percent oxygen content within a closed, dry, air-free reaction chamber, melting said magnesium and the condensed magnesium chloride within said chamber at a temperature ranging from 800–825° C. to provide direct contact between the resulting liquids which form and transfer of the oxygen present in said magnesium to the molten magnesium chloride, removing from said chamber the molten oxygen-containing magnesium chloride thus obtained and reacting the remaining purified oxygen-free magnesium in said chamber at an elevated temperature ranging from 850–950° C. and under an inert atmosphere with a chloride of a Fourth Group refractory metal to produce the corresponding refractory metal in a state of high purity.

3. A process for preparing titanium metal which comprises contacting solid, oxygen-containing magnesium having about a 0.01 to 0.04 weight percent oxygen content with vaporized, substantially oxygen-free magnesium chloride and condensing said vaporized magnesium chloride on the surface of said magnesium within a closed, dry, air-free reaction chamber, maintaining said chamber at temperatures ranging from above the melting point of magnesium chloride to substantially 1000° C. to effect melting of said magnesium and magnesium chloride in said chamber and direct contact between the two resulting liquid phases therein to permit oxygen present in said magnesium to transfer to said magnesium chloride, removing from said chamber the resulting oxygen-containing magnesium chloride and then reacting the purified oxygen-free magnesium which remains in said chamber with titanium tetrachloride, effecting said reaction under an inert atmosphere and at temperatures ranging from about 850–1000° C., and recovering the resulting pure titanium metal product.

4. An improved cyclic process for the preparation of a Fourth Group refractory metal by the reduction of a chloride of said refractory metal with molten magnesium, which comprises reacting at a temperature ranging from 750–1100° C. a refractory metal chloride with molten magnesium under inert atmosphere within a closed reaction vessel to produce said refractory metal and magnesium chloride by-product, separating at least a portion of said by-product magnesium chloride from the refractory metal product by vacuum distillation and condensation into an associated reaction vessel containing solid oxygen-contaminated magnesium metal containing about 0.01 to 0.04 weight percent oxygen, melting said solid magnesium and condensed magnesium chloride together in said associated vessel at a temperature ranging from above the melting point of MgCl to substantially 1000° C. to transfer the oxygen impurity present in said magnesium to said magnesium chloride, removing the resulting oxygen impurity-containing molten magnesium chloride from said associated reaction vessel and reacting under an inert atmosphere and elevated temperature ranging from 850–950° C. purified oxygen-free magnesium which remains in said associated vessel with a Fourth Group refractory metal chloride, separating a portion of the by-product magnesium chloride formed in said reaction and vacuum distilling and condensing it into an auxiliary reactor containing a charge of oxygen-contaminated magnesium, and recovering the pure refractory metal product formed in said associated reaction vessel.

5. An improved cyclic process for preparing titanium metal by reducing titanium tetrachloride with molten magnesium, comprising reacting titanium tetrachloride with molten magnesium under an inert atmosphere within a closed reaction vessel to produce titanium metal and magnesium chloride as a by-product, separating at least a portion of said magnesium chloride by-product from the titanium metal by vacuum distillation and condensation into an associated reaction vessel containing solid oxygen-contaminated magnesium metal, melting said solid magnesium and condensed magnesium chloride together in said associated vessel to transfer the oxygen impurity present in said magnesium to said magnesium chloride, removing the resulting oxygen impurity-containing molten magnesium chloride from said associated reaction vessel and reacting the purified oxygen-free magnesium remaining with titanium tetrachloride, effecting said reaction under an inert atmosphere and at temperatures ranging from about 850° C.–1000° C., separating a portion of the by-product magnesium chloride formed in said reaction and vacuum distilling and condensing it into an auxiliary reactor containing a charge of oxygen-contaminated magnesium, and recovering the pure titanium metal product formed in said associated reaction vessel.

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