



(86) Date de dépôt PCT/PCT Filing Date: 2008/01/16
(87) Date publication PCT/PCT Publication Date: 2008/07/31
(85) Entrée phase nationale/National Entry: 2009/07/22
(86) N° demande PCT/PCT Application No.: US 2008/051236
(87) N° publication PCT/PCT Publication No.: 2008/091773
(30) Priorités/Priorities: 2007/01/22 (US60/886,050);
2008/01/11 (US12/013,307)

(51) Cl.Int./Int.Cl. *C22B 34/12* (2006.01),
C22B 5/04 (2006.01), *C22B 5/14* (2006.01)
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(54) Titre : PRODUCTION EN CONTINU DE TITANE PAR LA REDUCTION METALLOTHERMIQUE DE TiCl_4
(54) Title: CONTINUOUS PRODUCTION OF TITANIUM BY THE METALLOTHERMIC REDUCTION OF TiCl_4

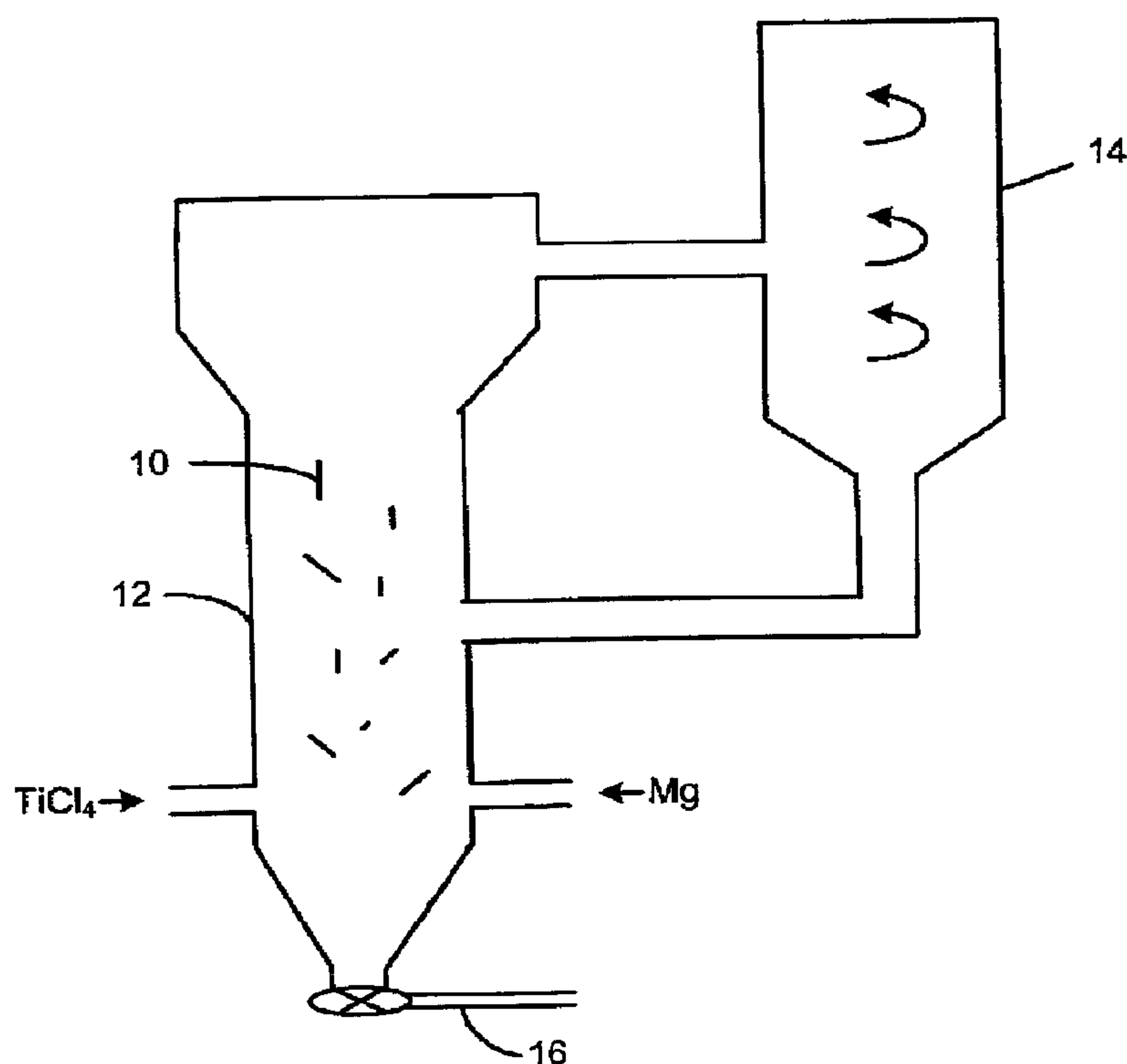


FIG. 1

(57) **Abrégé/Abstract:**

A method for production of titanium particles or other metal of interest by a metallothemic reduction reaction of TiCl_4 or other metal chloride in a reaction zone which comprises conducting the reaction in a fluidized bed reaction zone, and recycling particles to the reaction zone to build up particle size.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
31 July 2008 (31.07.2008)

PCT

(10) International Publication Number
WO 2008/091773 A1

(51) International Patent Classification:

B23K 35/00 (2006.01) **C21B 13/12** (2006.01)
C21B 11/10 (2006.01)

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(21) International Application Number:

PCT/US2008/051236

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(22) International Filing Date: 16 January 2008 (16.01.2008)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

60/886,050 22 January 2007 (22.01.2007) US
12/013,307 11 January 2008 (11.01.2008) US

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(81) **Designated States (unless otherwise indicated, for every kind of national protection available):** AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States (unless otherwise indicated, for every kind of regional protection available):** ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),

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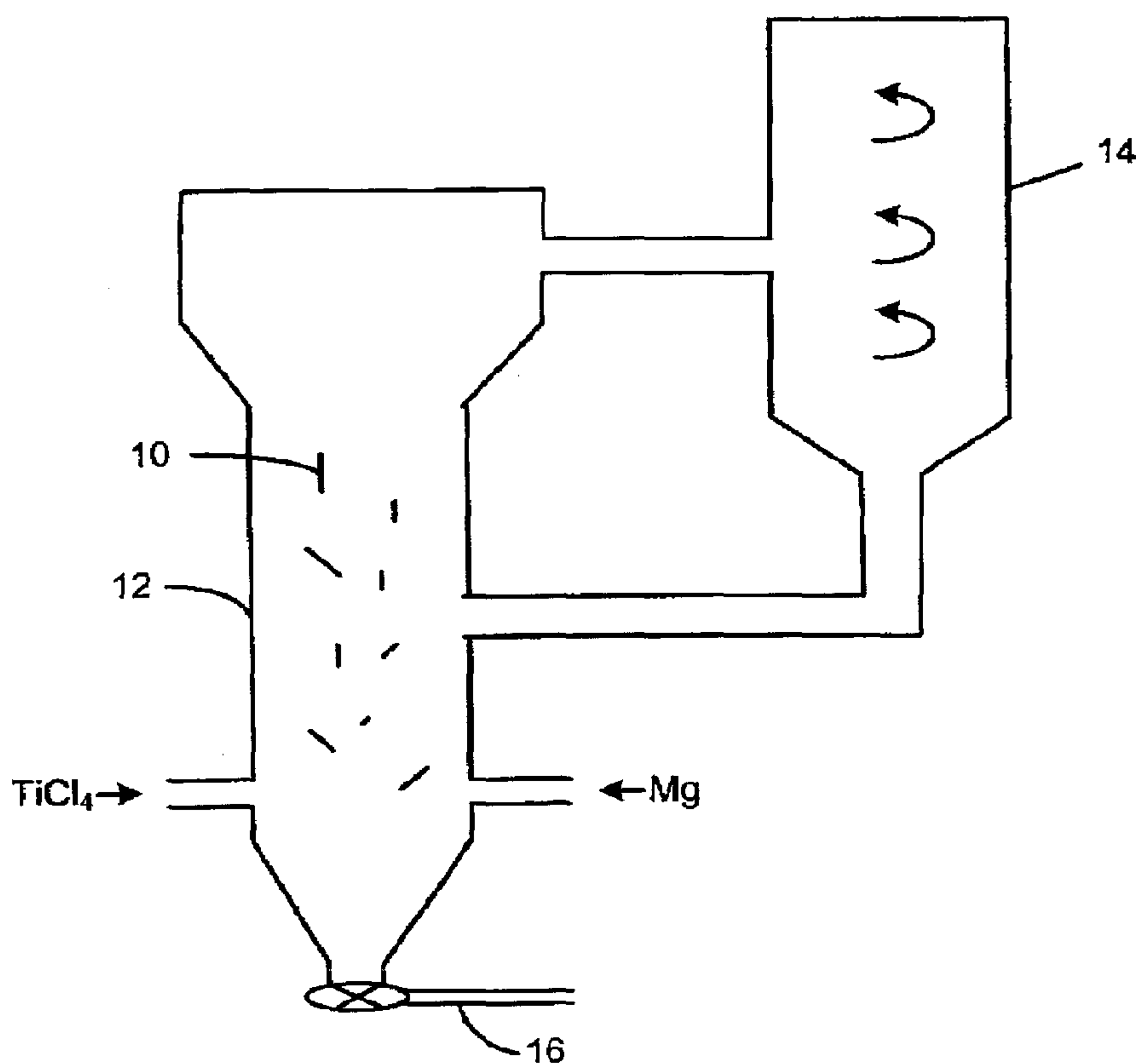
(54) Title: CONTINUOUS PRODUCTION OF TITANIUM BY THE METALLOTHERMIC REDUCTION OF TiCl_4 

FIG. 1

(57) **Abstract:** A method for production of titanium particles or other metal of interest by a metallothemic reduction reaction of TiCl_4 or other metal chloride in a reaction zone which comprises conducting the reaction in a fluidized bed reaction zone, and recycling particles to the reaction zone to build up particle size.

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European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI,
FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL,
NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG,
CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report*

Continuous Production of Titanium by the Metallothermic Reduction of TiCl_4

This invention relates to the production of metals. The invention has particular utility in connection with the production of titanium and will be described in connection
5 with such utility although other utilities are contemplated.

Substantially all the titanium produced throughout the world utilizes the magnesium reduction of titanium tetrachloride (TiCl_4) which is known as the Kroll process. The reaction is $2 \text{Mg}_{(l)} + \text{TiCl}_{4(g)} = \text{Ti}_{(s)} + 2\text{MgCl}_{2(l)}$. The process is typically carried out by bubbling TiCl_4 gas above liquid magnesium in a closed container operated
10 at approximately 800-1000°C (typically 900°C). Large steel containers are used to contain the molten magnesium in the absence of air. As the reaction proceeds, the magnesium chloride by-product is in a liquid state which is drained from the steel container. The titanium produced is in a sponge like morphology in a solid block. After substantially all the magnesium is consumed by the gaseous TiCl_4 , the process is stopped
15 and the solid titanium sponge is removed from the steel container after cooling to room temperature. The titanium sponge is broken up with jack hammers and separated into fractions, as the sponge in the bottom, sides, top and middle will exhibit different particulate size, shape and purity. This batch process is very labor intensive and the product titanium is not uniform. It has long been sought to produce the titanium
20 continuously and all product exhibit uniformity. The Kroll process to produce titanium has been practiced for approximately 50 years and no processing has emerged for continuous operation.

Others have investigated utilizing the fluid-bed concept to produce titanium. Hansen et al JOM, Nov. 1998, pgs. 56-58 report producing very small titanium particles
25 substantially less than 1 micron in diameter which cannot be exposed to the atmosphere without excessive oxygen pick-up or even explosion. However, new titanium did not form or deposit on existing particles as it was stated the by-product MgCl_2 condensed and coated the titanium particles that prevented any new growth on the particle at operation temperatures of 1000°C. Higher operation temperatures of 1500°C to vaporize
30 the MgCl_2 above its boiling point of 1412°C failed to produce useable titanium particles in the Hansen fluid-bed reactor. Hansen suggested titanium particles greater than 5 micron in diameter are necessary to prevent oxygen pick-up greater than acceptable to meet ASTM specifications.

Tisdale et al, in Titanium '95 Science and Technology, pgs. 1535-1542 report the vapor phase reaction of Mg and TiCl_4 at temperatures of 1150°C to 1425°C. Large excesses of Mg were required to prevent formation of TiCl_3 instead of or in addition to titanium. A high residence time of several seconds was required to provide the Mg
5 sufficient time to fully reduce the TiCl_4 all the way to titanium. The rates of the vapor phase reaction were five times that reported for the conventional Kroll reaction. Tisdale et al report producing both titanium particles as well as solid plating of titanium on hot surfaces. Small particle sizes were produced that required vacuum distillation to prevent oxygen pick-up from water washing or leaching to remove the by-product MgCl_2 which
10 lead Tisdale et al to suggest alternative methods were necessary to increase particle size to permit production of commercially viable titanium powder. The small particle size and solid plating results of Tisdale et al does not lend itself to continuous processing of commercially viable titanium.

British Patent No. 736,852, reports utilizing sodium, potassium or magnesium
15 vapors to reduce TiCl_4 vapors in a variety of apparatuses that produced spongy and molten titanium on the walls of the reactor chamber and the reducing metal halide by-product. However, continuous process of producing titanium powder was not achieved.

Worthington in US Patent No. 4,445,931 report molten sodium droplet sprayed into a vapor of TiCl_4 to produce titanium powder with NaCl by-product which was stated
20 could be practiced on a continuous basis.

Okudaira, et al in US Patent No. 4,877,445 report utilizing a fluid-bed seeded with titanium particles to which was fed vapors of magnesium and TiCl_4 operated at 50 Torr pressure and 1100°C. The low pressure and high temperature is said to cause vapor phase reaction of the Mg and TiCl_4 to produce titanium that grows onto the seeded
25 titanium particles. The vapor pressure of the by-product MgCl_2 is said to be 86 Torr which prevents condensing on the depositing titanium particles which allows them to build up in size. According to Okudaira et al the reactor is kept at a lower pressure to prevent any residual condensation of the by-product MgCl_2 into pores of the titanium particles. This lower pressure in the reactor prevents any flow of produced titanium
30 particles to a higher pressure container as alleged and shown in the drawing as well as contradicts that the larger titanium particles would exit a tube on the high side of the reactor in the illustration. The higher pressure in the outside container would prevent particles from flowing from a low to high pressure and the larger titanium particles would settle in the bed and not reach an exit tube located somewhere up the side of the

reactor as shown in the illustration. Maintaining the reaction vessel at 1100°C or above and a reduced pressure of 50 Torr could cause the reactor vessel to collapse if there is insufficient strength in the metal vessel at the low pressure and high temperature to prevent the vessel collapsing.

5 According to Okudaira et al only a small amount of titanium was produced on the walls of the reactor without the use of titanium particles as a seed in the bed. Since Okudaira et al requires titanium particle seeds in a fluid-bed in order to obtain deposition onto the seeds, the system is not continuous as the bed requires emptying when sufficient build up has occurred and a new seed put into place for new deposition and build up of
10 the particles.

 To achieve low cost production of titanium the process must be continuous and provide high production of titanium per unit volume of reactor. Another criteria is that no condensed liquid or solid phase interfere with the nucleation and growth of the only allowable solid phase titanium particles in the reaction zone. These criteria have been
15 met through unique design of reaction zones that don't require seeds to initiate the growth of particles but which provide for the build up of large titanium particles that eliminate high oxygen pick-up when exposed to air, and most importantly operation on a continuous basis to effect low cost production of titanium particulate. More particularly, in accordance with the present invention, there is provided a method for production of
20 titanium particles by metallothermic reduction reaction of TiCl_4 in a reaction zone which comprises conducting the reaction in a fluidized bed reaction zone, and recycling particles to the reaction zone to build up particle size.

 Alternatively, gaseous TiCl_4 and Mg may be reacted in a molten salt reactor wherein titanium will be produced either in particulate form or molten form, depending
25 on the temperature of the molten salt.

 Further features and advantages of the subjection invention will be seen from the following detailed description, taken in conjunction with the accompanying drawings, wherein like numerals depicts like parts, and wherein:

 Fig. 1 is a cross-sectional view illustrating a fluid-bed reactor for practicing the
30 present invention;

 Fig. 2 is a view similar to Fig. 1 showing an alternative fluid-bed reactor for practicing the present invention;

 Fig. 3 is a schematic view showing yet another embodiment of the present invention;

Fig. 4 is a cross-sectional view showing details of substrate useful in the practice of the Fig. 3 embodiment;

Fig. 5 is a schematic view showing yet another embodiment of the present invention;

5 Fig. 6 is a view similar to Fig. 1 of an alternative reaction system for practicing the present invention; and,

Fig. 7 is a view similar to Fig. 6 of yet another alternative embodiment of the present invention.

The present invention provides processes for the continuous synthesis of titanium
10 by magnesium reduction of TiCl_4 in the gaseous state. One embodiment of the invention titanium is produced continuously by mixing magnesium in the vapor or gaseous state with TiCl_4 vapor or gas in a particulate bed in which the particles are continuously in motion to avoid particle-to-particle agglomeration. In another
15 embodiment of the invention magnesium in the vapor or gaseous state is mixed with TiCl_4 vapor or gas in a high temperature molten salt such as calcium fluoride (CaF_2). Depending on the operating temperature of the molten salt such as CaF_2 , the titanium can be produced as a solid particulate or if the molten salt is operated above the melting point of titanium which is approximately 1670°C , the titanium will be produced in a molten or liquid state.

20 Referring to Fig. 1, in accordance with one embodiment of the invention, TiCl_4 and Mg vapors are introduced into the reaction zone 10 a fluid-bed reactor 12 where they react with homogenous nucleation that produces small particles, typically under one micron, which are collected in a series of cyclones 14 designed to collect such small particles at the velocity of the reactor gas flow. The small particles are recycled into the
25 fluid-bed reactor reaction zone 10 where they are built up through additional deposition from TiCl_4 and Mg vapor reaction. Recycle is continued until the particles grow to a desirable size range of, for example, 40 microns to 300 microns. As the particles become larger, they become heavier and settle to the bottom of the reactor, where they can be extracted by gravity flow through a pipe 16 connected to the bottom of the fluid
30 bed reactor. Thus, the formation of titanium in the reactor zone 10 is continuous and extraction of select size particles of titanium becomes continuous which results in low cost production of titanium.

As an alternative to collecting the small homogeneously nucleated titanium particles in a fluid-bed by cyclones we can utilize screens 18 over the top of the bed (see

Fig. 2) which prevent the particles from exiting, and vibrating the screen so that the small particles fall back into the reaction zone 10 which permits additional deposition until the particles are built up to a desired size. As before, as the particles become larger, they become heavier and settle in the bottom of the reactor, where they can be extracted by gravity flow through a pipe 16 connected to the bottom of the fluid-bed reactor. Preventing small particles from escaping from the reactor through the use of a fine screen 18 that causes the small particles to return into the reaction zone 10 permits the particles to be built up to a select size that are drained off from the bottom of the reactor thus permitting the fluidized-bed to be operated on a continuous basis.

With small particles being initially produced in a fluid-bed and deposition building up larger particles that also must be fluidized or at least bumped to move sufficiently to prevent particles from agglomerating, in order to maintain a gas flow through the fluid-bed that does not blow small particles out of the reactor yet keep moving the larger particles, in a preferred embodiment of the invention we have found it desirable to pulse the gas flow. That way we can keep the larger particles from agglomerating, while not blowing the small particles out of the reactor. Thus, by pulsing the gas flow, coupled with screening and/or cyclones separation to return the small particles to the reaction zone, continuous deposition and build up of the particles, is achieved, whereupon the system can be operated continuously.

Alternatively, since the gas flow in a fluidized-bed can present a problem with maintaining idealized fluidization with diverse particle sizes in the bed, another possibility, illustrated in Fig. 3 is to deposit the titanium onto a substrate 20 having a desired geometric shape that produces the desired particle morphology. The substrate 20 is moved through the reaction zone 10 and the deposited titanium can then be removed from the deposition surface by scraping and/or flexing or bending at release station 22 to remove the deposited titanium from the surface onto which it was deposited. Substrate 20 may comprise a titanium wire screen or a titanium sheet has a contoured surface formed, for example, by machining or etching, to a geometric shape that is desired for the deposited particles, for example half round columns 24 (see Fig. 4). Another approach to forming the substrate 20, shown in Fig. 5, is to selectively bundle together a plurality of wires 26 with their ends 28 facing the deposition zone in which titanium will be deposited on the ends of the wires and the deposit removed by passing the wires under a blade 30 that removes or scrapes off the deposited titanium. The deposition substrate may be moved through the deposition zone in a step-wise or continuously, whereby

titanium may be removed as it is produced by the reaction of magnesium and TiCl_4 vapors, under temperature and pressure conditions such that no liquid can condense on the surface of the substrate.

Yet another alternative embodiment is illustrated in Fig. 6, in which we mix
5 gaseous magnesium vapors with TiCl_4 gas within a reactor 30 containing molten salt bath 32 such as CaF_2 . The temperature of the molten salt bath 32 should be sufficiently high to maintain the magnesium in a gaseous state. At atmospheric pressure within the molten salt bath 32, magnesium boils at approximately $1097\text{--}1107^\circ\text{C}$. Thus the molten salt bath 32 should be operated to at least the boiling point of magnesium. The by-
10 product of the reaction is MgCl_2 which should be continuously removed from the molten salt bath as a vapor. MgCl_2 boils at approximately 1412°C . Thus if the molten salt bath such as CaF_2 is operated at above 1412°C the magnesium chloride will continuously boil and vaporize out of the molten salt bath where the MgCl_2 vapor may be collected and recycled for electrolysis to produce more magnesium reductant feed.

15 At temperatures less than the melting point of titanium when the gaseous Mg and TiCl_4 react, particles of titanium are produced which sink to the bottom of the molten salt bath since titanium is heavier than molten salts such as CaF_2 . The solid particles of titanium can then be siphoned from the bottom of the reactor using, for example, gas pumping or a negative pressure pump 34. As before the by-product is MgCl_2 which will
20 vaporize in the molten salt bath provided the bath is operated above the boiling point of MgCl_2 , i.e. above 1412°C , which vapor can be collected and recycled for electrolysis to produce the required magnesium reductant feed. Yet another alternative embodiment is illustrated in Fig. 7. Here the molten salt bath, such as CaF_2 , is operated above the melting point of titanium (approximately 1670°C). Under these conditions the reaction
25 between magnesium and TiCl_4 vapor produces titanium in a molten state. The molten titanium is then withdrawn from the reactor, passed through to freeze zone 36, and removed as a solid ingot on a continuous basis.

While the invention has been described in connection with the production of titanium, other high value metals of interest such as chromium, hafnium, molybdenum,
30 niobium, tantalum, tungsten, vanadium and zirconium may be produced by metallothermic reduction of the corresponding chloride in the gaseous state to produce the metal of interest.

Yet other changes may be made without departing from the spirit and scope of the invention.

What is claimed is:

1. A method for the production of titanium by the metallothermic reduction reaction of TiCl_4 in gaseous state, which comprises conducting the reaction in a fluidized bed reaction zone to produce titanium particles, and recycling particles to the reaction zone to build up particle size.
5
2. The method of claim 1, comprising withdrawing titanium particles from the reaction zone once they achieve a pre-determined size.
3. The method of claim 1, which comprises collecting the particles on a substrate, and vibrating or flexing the substrate so that particles fall back into the reaction zone until the particles are built up to a pre-determined size.
10
4. The method of claim 3, wherein the substrate comprises a screen or sheet.
5. The method of claim 3, wherein the screen or sheet is formed of titanium.
6. The method of claim 3, wherein the sheet has a contoured surface.
7. The method of claim 6, wherein the contoured surface is formed by
15 machining or etching.
8. The method of claim 6, wherein the sheet has a plurality of half-round columns formed in a surface thereof.
9. The method of claim 1, wherein the particles are deposited on a substrate, and including the step of scraping the deposit from the substrate.
- 20 10. The method of claim 9, wherein the substrate comprises a bundle of wires, and the particles are deposited on the ends of the wires.
11. The method of claim 1, wherein the fluidized bed is pulse fluidized.
12. A method for the production of titanium which comprises reacting gaseous TiCl_4 and Mg in a molten salt reactor.
- 25 13. The method of claim 12, wherein the titanium produced is in a molten state, and including the steps of solidifying the molten titanium by passing the molten titanium to a cooling zone, and collecting the solidified titanium from the cooling zone.
14. The method of claim 12, wherein the titanium is produced as solid particles, and including the step of removing the solid particles from the molten salt
30 reactor.
15. The method of claim 12, wherein the molten salt comprises calcium fluoride.

16. The method of claim 12, wherein MgCl_2 is produced as a by-product, and including the steps of passing the by-product MgCl_2 to electrodialysis where the Mg is recovered and recycled to the molten salt reactor.

17. The method for the production of a metal of interest by metallothermic
5 reduction reaction of a metal chloride in a gaseous state, which comprises conducting the reaction in a fluidized bed reaction zone to form particles of the metal of interest, and recycling particles to the reaction zone to build up particle size; wherein the metal of interest is selected from the group consisting of the chromium, hafnium, molybdenum, niobium tantalum, tungsten, vanadium and zirconium.

10 18. The method of claim 17, comprising withdrawing metal particles of interest from the reaction zone once they achieve a pre-determined size.

19. The method of claim 17, which comprises collecting the particles on a substrate, and vibrating or flexing the substrate so that particles fall back into the reaction zone until the particles are built up to a pre-determined size.

15 20. The method of claim 19, wherein the substrate comprises a screen or sheet.

21. The method of claim 19, wherein the screen or sheet is formed of the metal of interest.

22. The method of claim 19, wherein the sheet has a contoured surface.

20 23. The method of claim 22, wherein the contoured surface is formed by machining or etching.

24. The method of claim 22, wherein the sheet has a plurality of half-round columns formed in a surface thereof.

25. The method of claim 17, wherein the fluidized bed is pulse fluidized.

25 26. The method of claim 17, wherein the particles are deposited on a substrate, and including the step of scraping the deposit from the substrate.

27. The method of claim 26, wherein the substrate comprises a bundle of wires, and the particles are deposited on the ends of the wires.

28. The method of claim 27, wherein the metal of interest is produced in a
30 molten state, and including the steps of solidifying the molten metal of interest by passing the molten metal of interest to a cooling zone, and collecting the solidified metal of interest from the cooling zone.

29. The method of claim 17, wherein the fluid bed is pulse fluidized.

30. A method for the production of a metal of interest which comprises reacting Mg and a chloride of the metal of interest in a gaseous state in a molten salt reactor, wherein the metal of interest is selected from the group consisting of chromium, hafnium, molybdenum, niobium, tantalum, tungsten, vanadium and zirconium.

5 31. The method of claim 30, wherein the metal of interest is produced as solid particles, and including the step of removing the solid particles from the molten salt reactor.

32. The method of claim 30, wherein the molten salt comprises calcium fluoride.

10 33. The method of claim 30, wherein MgCl_2 is produced as a by-product, and including the step of passing the by-product MgCl_2 to electrodialysis where the Mg is recovered and recycled to the molten salt reactor.

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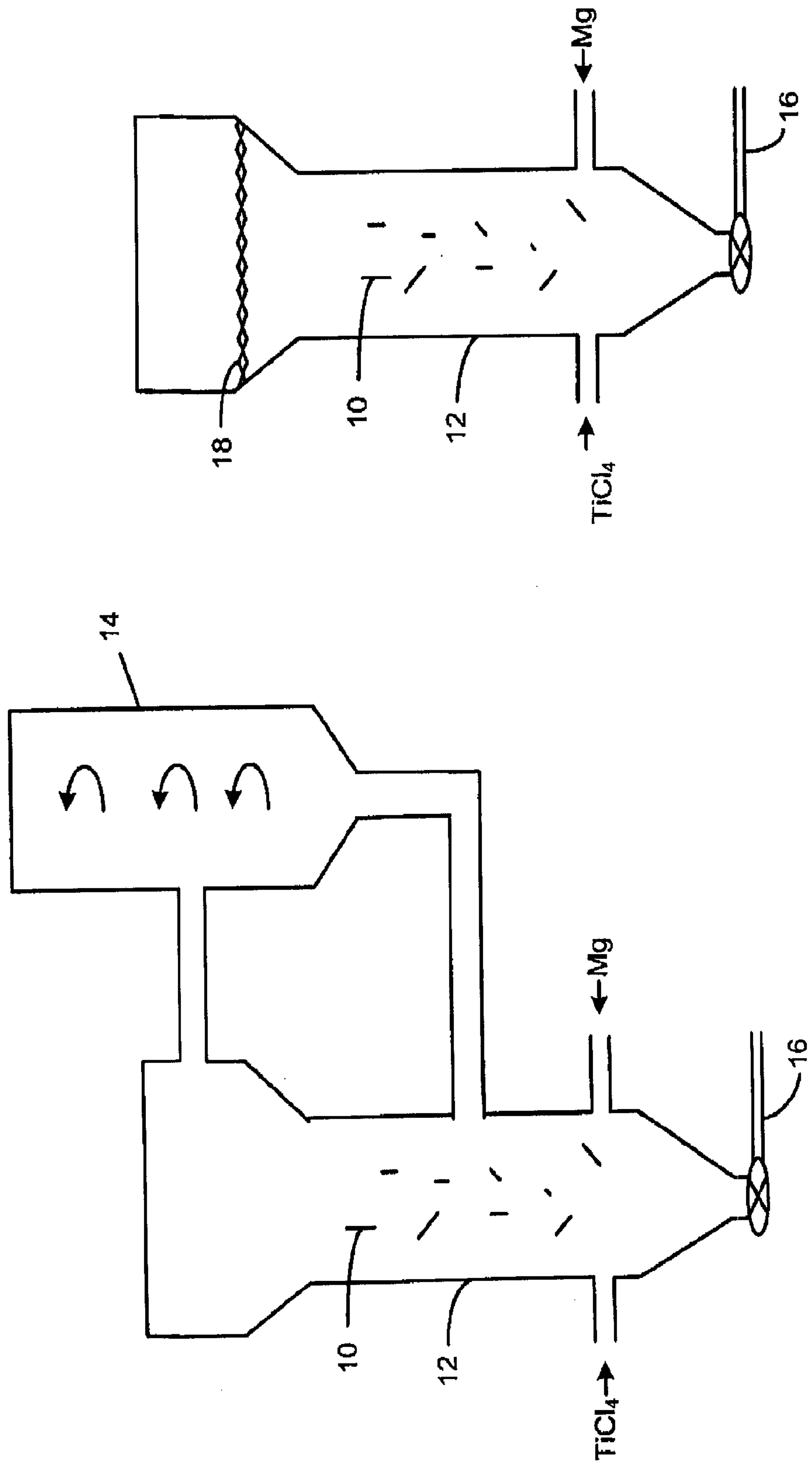


FIG. 2

FIG. 1

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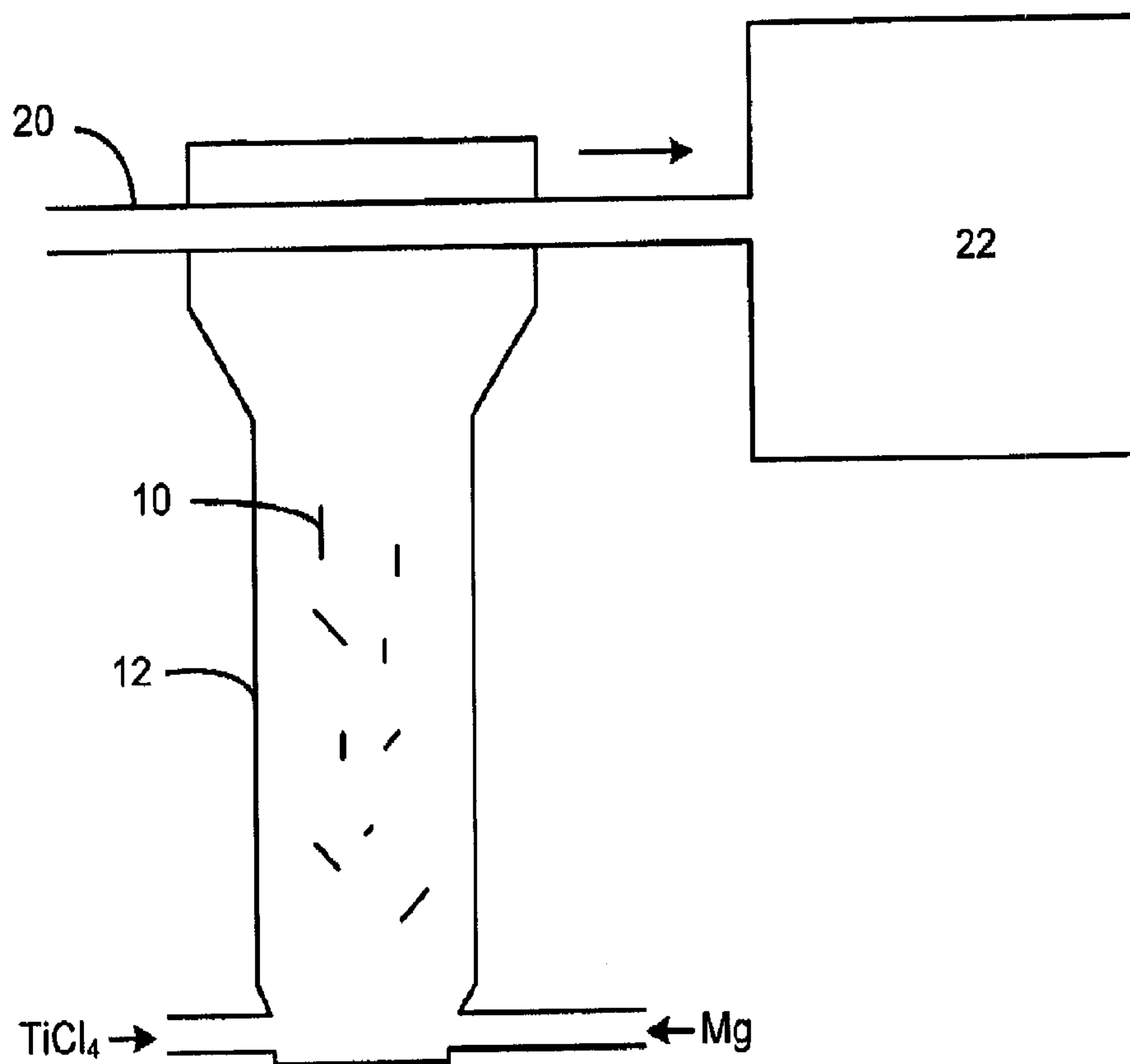


FIG. 3

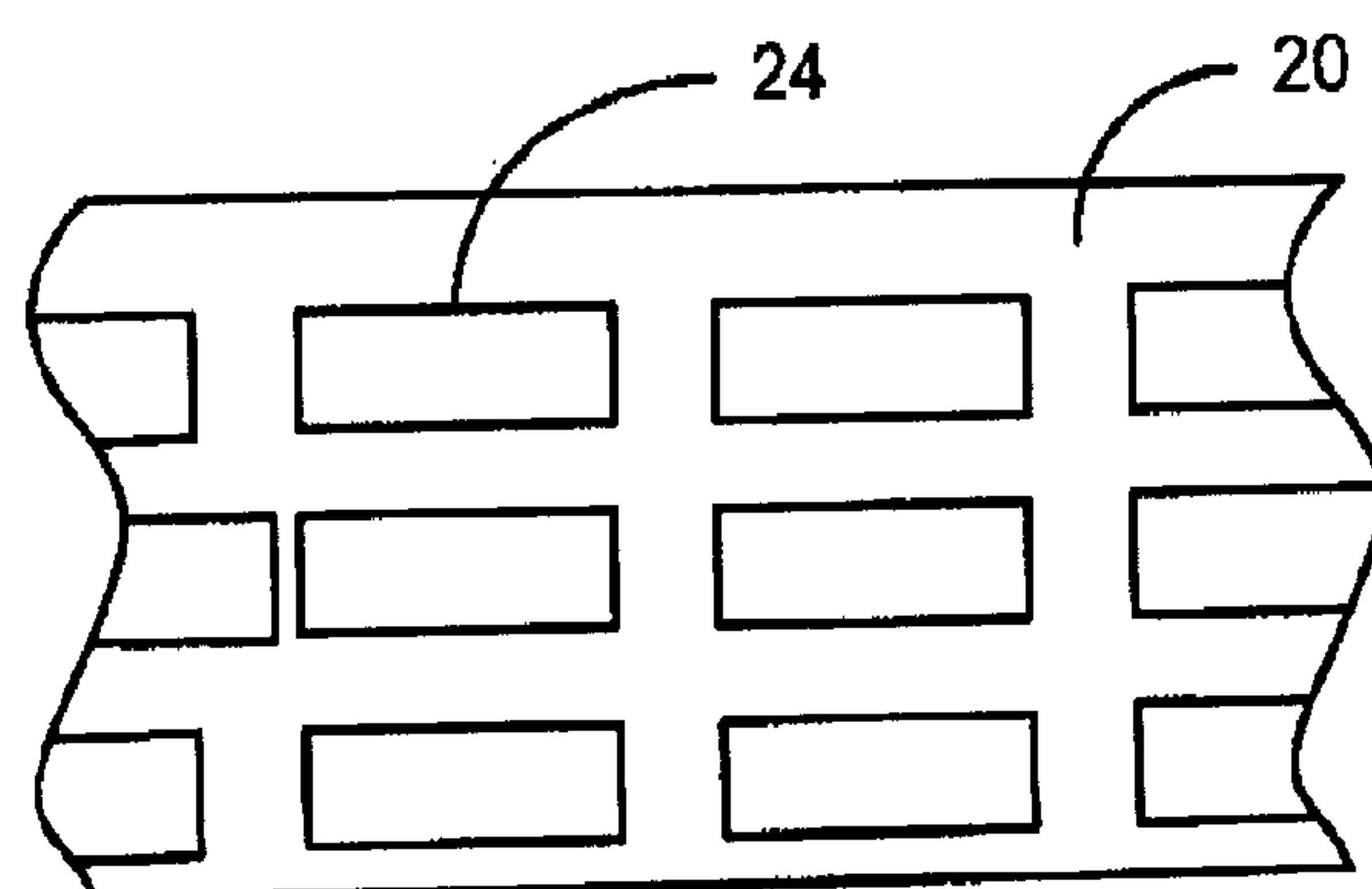


FIG. 4

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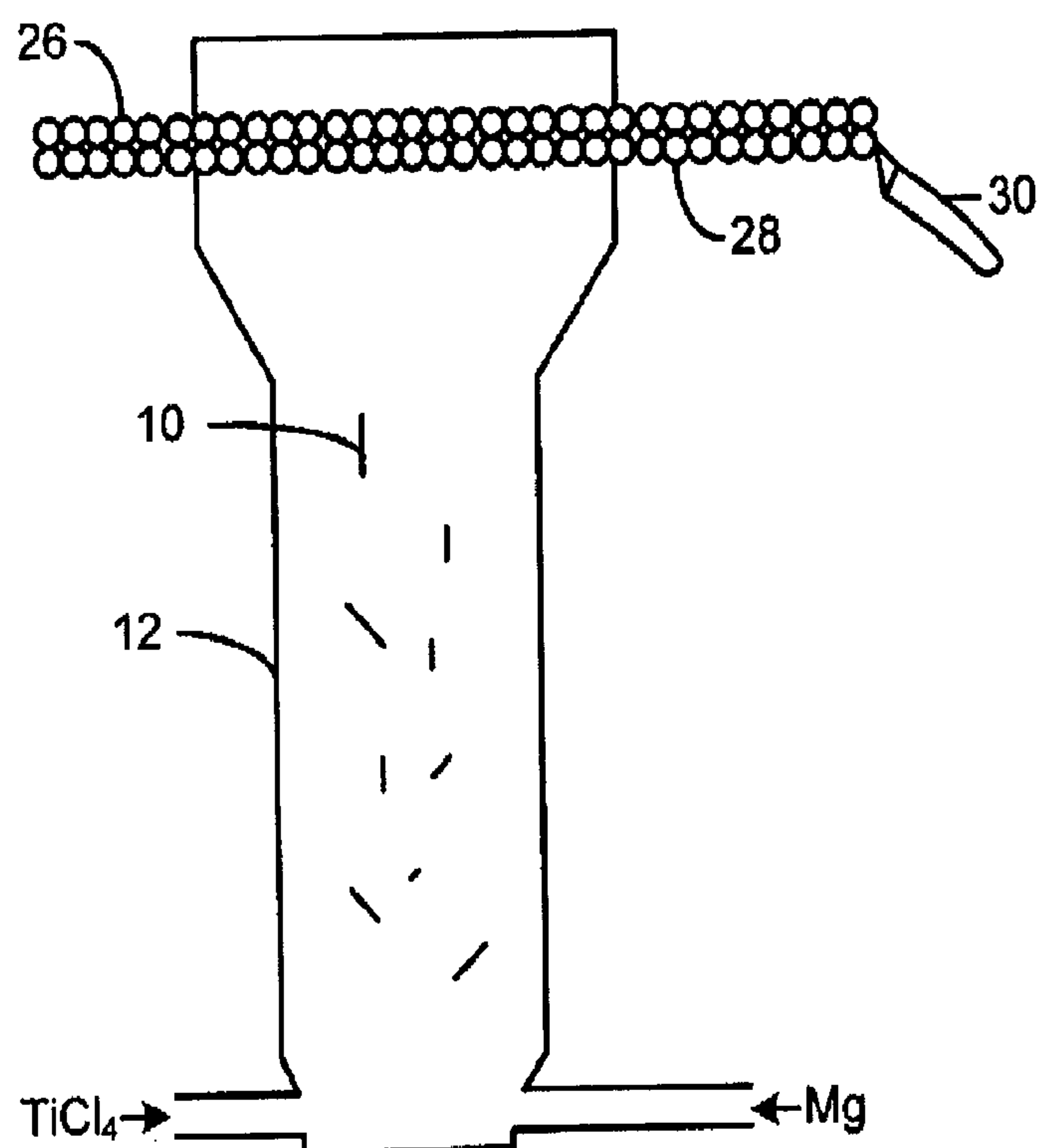


FIG. 5

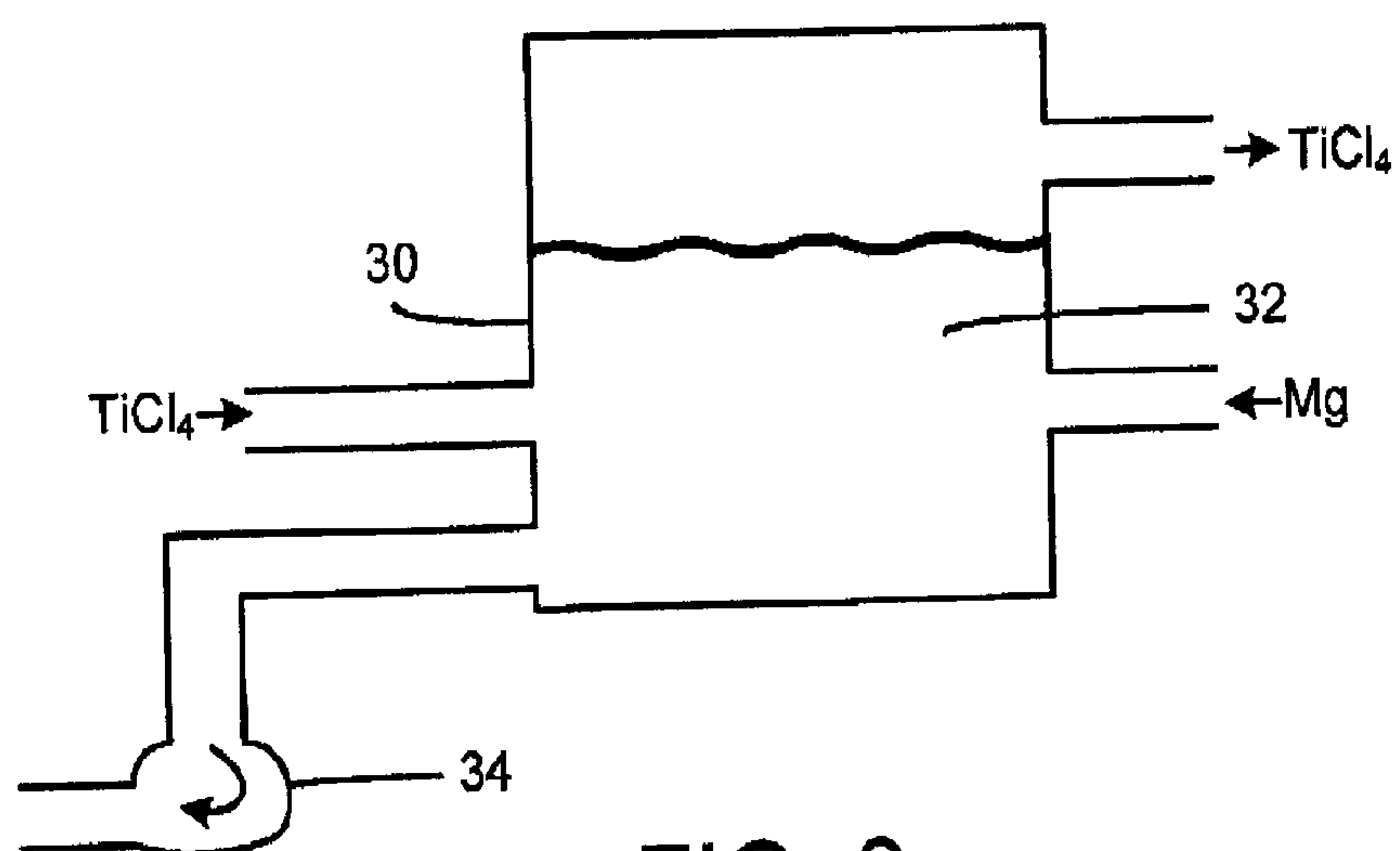


FIG. 6

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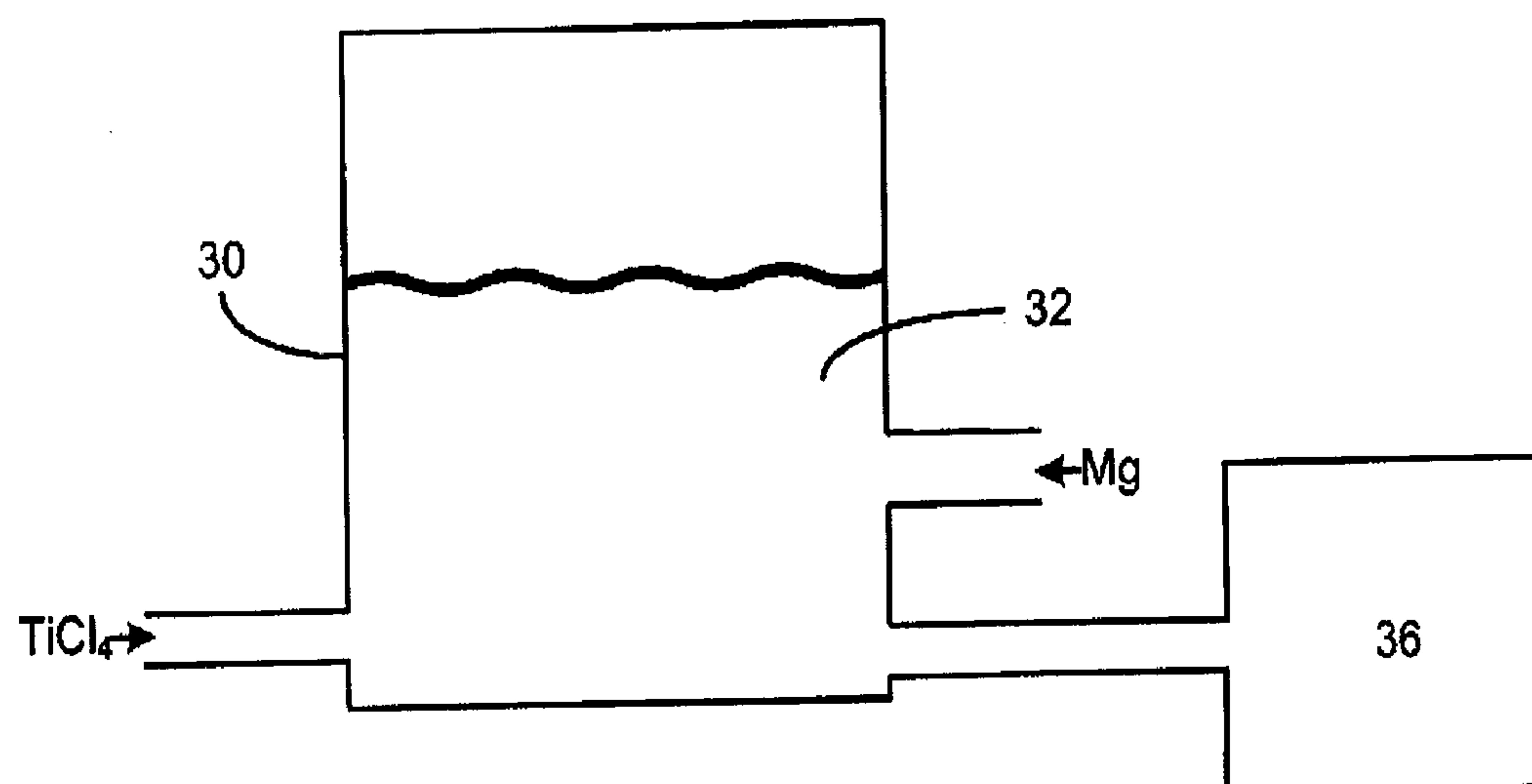


FIG. 7

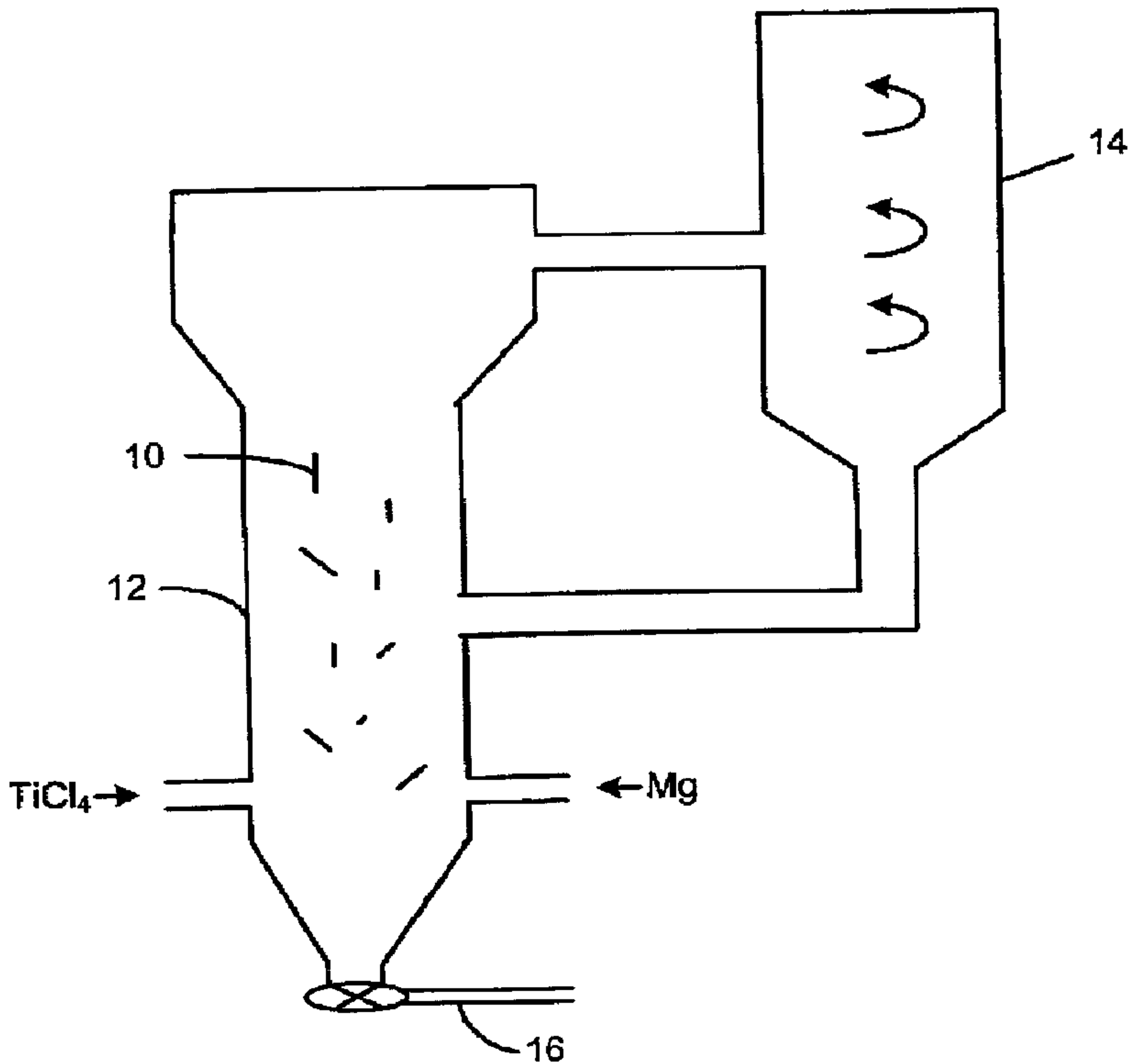


FIG. 1