Feb. 20, 1962 D. S. CHISHOLM ETAL 3,021,562

PRODUCTION OF GROUP IV, SUBGROUP A, METAL PRILLS

Filed April 1, 1957

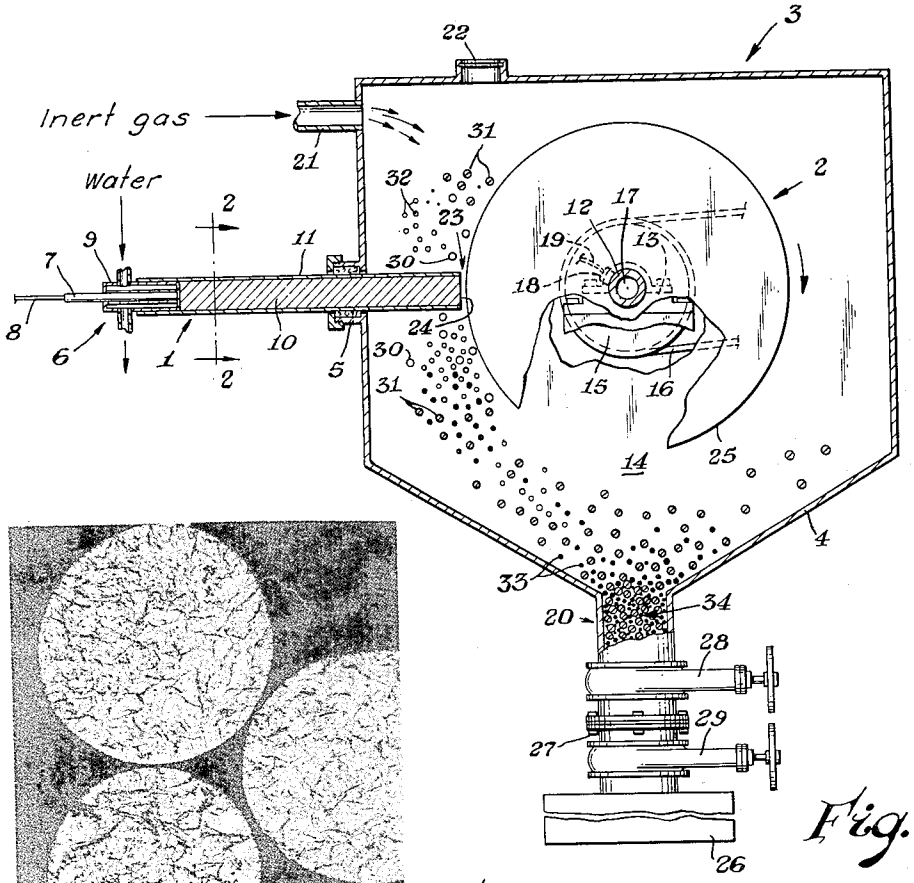


Fig. 1

Fig. 4

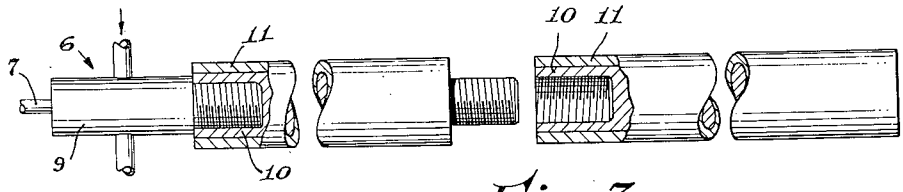


Fig. 3

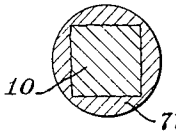


Fig. 2

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United States Patent Office 3,021,562 Patented Feb. 20, 1962

3,021,562
PRODUCTION OF GROUP IV, SUBGROUP A, METAL PRILLS

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Filed Apr. 1, 1957, Ser. No. 649,809
10 Claims. (Cl. 18—47.2)

The invention is directed toward the production of a substantially pure ductile metal of group IV, subgroup *a*, of the periodic table of elements from an impure form thereof. It is particularly directed toward the production of such a metal in the form of prills by the electric arc-melting of impure ingots containing the metal.

Heretofore group IV, subgroup *a*, metals, hereinafter referred to as subgroup IV*a*, viz., titanium, zirconium, hafnium, and thorium, have been produced largely as a sponge by the reduction of a halide of the metal to be produced in an atmosphere of an inert gas, e.g., helium or argon, by a metal more electropositive than the metal to be produced, e.g., magnesium, sodium, or calcium. Thus produced, the sponge contains undesirable impurities. These impurities render the metal brittle and unsuitable without purification for alloying and frabrication.

Substantially pure metals of subgroup IV*a* metals can be produced by reacting the impure metal with iodine to form the tetraiodide and thereafter thermally dissociating the tetraiodide by bringing it into contact with a hot metal filament, e.g., tungsten or titanium, upon which the metal to be produced is deposited and from which the iodine is volatilized. The filament is thereafter cooled and the subgroup IV*a* metal thus deposited is scraped therefrom. The process is slow and expensive. Except for the preparation of a subgroup IV*a* metal for highly specialized uses, the tetraiodide dissociation process is not economical.

Therefore, the production of the subgroup IV*a* metals from their halides by a reducing metal, such as magnesium, is currently in wide use although encumbered by a number of disadvantages. An improved method of reducing a subgroup IV*a* metal from its halide by the action of magnesium and recovering the metal, e.g., titanium or zirconium, is described in British Patent 734,166 and in our copending United States application, Ser. No. 315,604, filed October 20, 1952, now Patent No. 2,840,465. In a second of our copending United States applications, Serial No. 653,391, filed April 17, 1957, now Patent No. 2,932,565, there is described an improved method of recovering the metal sponge produced according to British Patent 734,166 or copending application No. 315,604. According to the second of the above identified copending applications, an ingot is produced comprising a core predominantly of the metal sponge being produced incased in a protective sheath predominantly of the halide of the reducing metal. The balance of the core is substantially the halide of the reducing metal, and the balance of the sheath is substantially the metal sponge being produced. At least 50 percent of the ingot consists of the metal being produced. A core largely of titanium metal incased in a sheath largely of $MgCl_2$ will illustrate an ingot thus formed.

Ductile metals of subgroup IV*a*, e.g., zirconium and titanium, in alloyed form are particularly suited to a wide number of uses requiring an alloyed metal of high strength, medium weight, and excellent corrosion resistance. An example of such a use is in the manufacture of specific structural aeroplane parts. Titanium or zirconium sponge made by methods currently in general use must be refined or purified before it can satisfactorily meet the specifications required for alloys of such metals.

An object of the invention is to provide a method of producing a substantially pure metal of subgroups IV*a* from an impure form thereof.

Another object is to produce a novel form of such substantially pure metal having the general shape of spheroids, herein referred to as prills.

A further object is to provide a method of producing such metals which utilizes electric-arc melting of a feed stick or ingot comprising a core of the metal to be produced protected both from air before entering the arc chamber and from the titanium tetrachloride vapors in the arc chamber by a sheath of a metal halide about the core.

A still further object is to produce a metal of subgroup IV*a* in the form of ductile prills which may subsequently be simultaneously compacted and resistance-sintered or welded into continuous rod for use as consumable electrodes for alloying.

A still further object is to provide a continuous method of producing ductile metals of subgroup IV*a* which is more efficient and economical than methods now known.

These and other objects of the invention will be made clear by the following description of the invention together with the appended claims and annexed drawing.

The invention is based upon the discovery that substantially pure subgroup IV*a* metal prills are produced from an impure form thereof when an electric arc is struck in an atmosphere of an inert gas between two electrode rods or ingots which are predominantly of the metal to be produced and one of which is rotating.

The invention is therefore directed to the novel method of producing a product consisting of substantially pure subgroup IV*a* prills. The method broadly consists of positioning two electrodes consisting of at least 50 percent of the subgroup IV*a* metal to be converted into prills in an arc chamber, containing an inert gas, in such manner that a first electrode is rotatable and a second electrode is advanceable toward the first electrode, rotating the first electrode and advancing the second toward it so as to strike an arc between the two electrodes on applying a suitable current to them. Although the cross-section of the advanceable electrode may be of any substantially symmetrical shape, it is preferred that it be cylindriform. The rotatable electrode should be cylindriform and positioned so that it undergoes no substantial translatory motion.

The advanceable electrode must be of the impure subgroup IV*a* metal to be converted into substantially pure metal. The metal of the rotating electrode may be alike or similar to that of the electrode advanceable toward it or it may be substantially of the pure subgroup IV*a* metal to be produced. It is preferred that it be substantially pure metal for reasons to be pointed out hereinafter. The subgroup IV*a*-bearing electrodes are positioned in a non-parallel relationship so that their longitudinal axes form angles greater than 0° and less than 180° to each other, but an angle of say 30° to 90° gives better results than one approaching an angle of 180°.

According to the preferred mode of practicing the invention, the angle formed between the longitudinal axes should be about 90°, i.e., the advanceable electrode should be positioned substantially radially of the rotating electrode. It is also preferred that the arc be formed between the arcuate surface, near one end of the rotating electrode, and the nose of the advanceable electrode. If the arc is struck too far back from either of the ends of the rotating electrode, the electrode becomes grooved and may melt through causing the portion thereof which extends beyond the arc to drop off. The rotating electrode may be elongated, but it is advantageous to have its disc-like, i.e., its diameter large in comparison to its longitudinal axis. It is also advantageous to have the rotating

electrode of greater circumference than the advanceable electrode positioned generally radially thereof so that greater peripheral speed may be attained at a given angular speed. Successful operation permits a wide range of rate of rotation. An angular rate of rotation which results in a peripheral speed of the rotatable electrode of between 10 and 100 feet per second is usually employed.

Another mode of practicing the invention is to rotate both electrodes, either in opposite directions or in the same direction at different speeds. Still another mode is to oscillate the spatially stationary electrode by causing it to rotate, preferably through 360°, in one direction and then in the reverse direction an equal number of degrees.

FIGURE 1 shows an elevation partly in section of an apparatus suitable for practicing the invention.

FIGURE 2 shows a cross-section of a rod or ingot of an impure subgroup IV*a* metal, e.g., titanium, made according to copending application Serial No. 653,391, suitable as the consumable electrode for use in the invention. It consists of a core **10**, more or less rectangular in cross-section, consisting of roughly 80 to 90 percent metal sponge incased in cylindriform sheath **11** consisting of about 80 to 90 percent of the halide of the reducing metal.

FIGURE 3 shows sections of a consumable electrode of impure subgroup IV*a* metal placed end-to-end suitable for threaded engagement for continuous operation according to the invention.

FIGURE 4 shows a photomicrograph (magnification of 100 diameters) of sectioned prills formed according to the invention.

Since an ingot consisting of a core predominantly of titanium and a sheath predominantly of $MgCl_2$ best typifies the material employed in the practice of the invention, the invention will be illustrated by the use of such an ingot.

Referring to the drawing in more detail, FIGURE 1 shows an apparatus suitable for practicing a preferred mode of the invention. It comprises advanceable consumable electrode **1** of impure titanium, rotating electrode **2**, and cylindrical arc-chamber **3** provided with conical bottom **4**, droptube **20**, inert gas inlet **21**, observation window **22**, and suitaby located openings for the operation of electrodes **2** and **3**.

Electrode **1** passes through stuffing box **5** inserted in the opening provided therefor in the wall of chamber **3** and made advanceable radially of electrode **2** near the foremost nose thereof to form gap **23** between nose **24** of electrode **1** and arcuate surface **25** of electrode **2**. Copper nipple **6** contains electrical terminal **7** which is connected to lead-in line **8** leading to a source of D.C. or A.C. Water jacket **9** about nipple **6** is provided with water for cooling nipple **6**. Electrode **1** is composed of core **10** and outer protective sheath **11**.

Rotating electrode **2** is secured to shaft **12**. Shaft **12** is positioned substantially horizontally and transversely in chamber **3** at right angles to electrode **1**. It is journaled in front and rear bearings **13**, only the rear one of which is shown supported just outside of chamber wall **14**. Shaft **12** is rotated by pulley **15** turned by belt **16** which is powered by a source not shown. Shaft **12** is provided with central channel **17** through which is circulated a cooling fluid. Shaft **12** also serves as an electrical terminal, being connected by brush **18** to lead-in line **19** which leads from the opposite pole of the source of electricity connected to lead-in line **8**.

Receiver **26** is shown removably affixed to drop tube **20** by means of bolts **27**. Valve **28** in droptube **20** and valve **29** in receiver **26** control the flow of reaction product from droptube **20** into receiver **26**.

In practicing the invention according to the preferred mode of operation, inert gas is introduced through inlet **21** to flush out chamber **3** and to maintain an atmosphere comprising the inert gas in the chamber. Lead-in lines **8** and **19** are connected to the opposite poles of a source of D.C. or A.C. The voltage is not critical. A 60 volt D.C. and a 100 volt A.C. have proved satisfactory. Consumable electrode **1** of an impure subgroup IV*a* metal contaminated with a halide of a reducing metal is advanced substantially radially of rotating electrode **2** which is of the same subgroup IV*a* metal as advancing electrode **1**, but which is in a substantially pure state, so as to strike an arc in gap **23** formed between nose **24** of electrode **1** and arcuate surface **25** of electrode **2**.

The proper positioning of electrode **1** to attain the desired arc may be aided by observing gap **23** through observation window **22**. A suitable arc is usually obtained when the width of gap **23** is about ⅛ inch.

The heat provided by the arc melts and/or vaporizes electrode **1** at nose **24** so that it is gradually and continuously consumed. Electrode **1** is, therefore, advanced either manually or automatically toward electrode **2**. The metal is caused to fly from the arc as small globules **30** and the halide salt either as vapor or droplets, both of which thereafter solidfy. The moving surface of rotating electrode **2** dissipates the heat so that the melting point of rotating electrode **2** is not reached. Melting is therefore confined to non-rotating electrode **1**. Furthermore, when the rotating electrode **2** is of substantially pure metal, its conductivity is higher and therefore its temperature at the arc is somewhat lower than that of the less pure metal.

It is preferable that electrode **2** rotate clockwise as shown in FIGURE 1 to impel a large portion of the molten titanium and the halide salt upwardly so as to allow an added time to solidify before their striking the body of reaction product **34** at the bottom of chamber **3**. It has been observed, however, that all particles of molten metal leaving the arc solidify into prills **31** within about 12 inches of the arc. It is thought that the halide first forms as a vapor, condenses into droplets **32** upon leaving the vicinity of the arc, and thereafter solidifies into granules **33**. The granules **33** and prills **31** fall into conical bottom **4** of chamber **3** to form flowable reaction product **34** composed of a mixture of the granules and prills. The dissipation of heat from the apparatus is usually sufficient to cause halide droplets **32** to solidify before becoming part of reaction product **34**, but if desired, cooling coils may be placed about conical bottom **4** to aid in cooling.

By opening valves **28** and **29**, reaction product **34** is dropped into receiver **26**. Periodically valves **28** and **29** may be closed and bolts **27** removed, thus disengaging receiver **26** without admission of air. Receiver **26** is then either removed to a place of storage and replaced by another similar receiver, or the contents properly disposed of and receiver **26** again affixed to droptube **20**. Valves **28** and **29** are again opened.

Prills **31** are thereafter separated from the magnesium chloride by known methods as by dissolving the chloride in water, collecting the prills on a suitable mesh sieve, e.g., a 100 mesh sieve (Standard Sieve of United States Bureau of Standard Series), and washing with water and drying.

The prills thus formed, from which the magnesium chloride has been separated, are substantially pure titanium. They have an average bulk density of about 3 grams per cubic centimeter. They are of a size that at least 95 percent thereof will pass through a No. 6 sieve and be retained on a No. 200. They have a Brinell hardness number of between 130 and 200.

They may be compressed into blocks or shapes. However, they are most advantageously employed in the preparation of consumable electrodes for alloying subgroup IV*a* metals by subjecting a mass of the prills to pressure and simultaneously passing electric current through the mass to effect a welding together of the individual prills to form consumable electrodes. A method by which particles of subgroup IV*a* metals may be made into coherent massive metal suitable for use as a consumable

electrode is by the application of the principle described in "Resistance Sintering Under Pressure" in Journal of Metals, pages 158 to 167 (January 1955). If desired, the operation may be a continuous process. A convenient method by which the operation described therein may be made continuous to produce rods is described in Trans. of Am. Inst. of Mining and Metallurgical Engineers, vol. 171, Inst. of Metals Div., pages 416 to 430 (1946), wherein a collet serves both as a means for providing the proper frictional resistance to the pressure imposed by a plunger electrode on confined metal particles and as an electrode of opposite polarity to the plunger.

Although the practice of the invention has been described for the use of an ingot composed of a predominantly titanium core incased in a predominantly $MgCl_2$ sheath, the invention is applicable to the production of any subgroup IV*a* metal from an impure consumable electrode containing at least 50 percent of the metal to be produced.

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

1. The method of making ductile prills of a group IV, subgroup *a*, metal selected from the class consisting of titanium, zirconium, thorium and hafnium which comprises striking an electric arc in an atmosphere of an inert gas between the nose of an advanceable, consumable electrode consisting of at least 50 percent of the metal being produced and a rotating cylindriform electrode of a metal having a melting point at least as high as the metal being produced, said electrodes being positioned so that their longitudinal axes are substantially horizontal and form angles therebetween, each of said angles being less than 180°.

2. The method of making substantially solid spheroidal prills of a group IV, subgroup *a*, ductile metal selected from the class consisting of titanium, zirconium, thorium and hafnium, which comprises striking an electric arc between the circumferential periphery of a rotating cylindriform electrode consisting at least of 50 percent of the group IV, subgroup *a*, metal being produced and the nose of an elongated consumable, substantially horizontal electrode advanceable toward the rotating electrode, comprising the same said group IV, subgroup *a*, metal in an impure state, the longitudinal axis of said advanceable electrode being disposed to form angles, each of which is less than 180° with the longitudinal axis of said rotating electrode, the nose of said advanceable electrode being positioned adjacent to but not touching the periphery of said rotating electrode to maintain said electric arc.

3. The method according to claim 2 wherein the group IV, subgroup *a*, metal is titanium.

4. The method according to 2 wherein the metal of the advanceable electrode contains magnesium chloride.

5. The method according to claim 2 wherein both electrodes comprise a metal sponge of group IV, subgroup *a*, and a halide of a metal more electropositive than titanium.

6. The method according to claim 2 wherein said rotatable electrode is substantially the pure metal of group IV, subgroup *a*, being produced.

7. The method according to claim 2 wherein said advanceable electrode consists essentially of a predominantly titanium sponge core incased in a predominantly magnesium chloride sheath.

8. The method according to claim 2 wherein said advanceable electrode consists essentially of a predominantly zirconium sponge core incased in a predominantly magnesium chloride sheath.

9. The method according to claim 2 wherein the said advanceable electrode is positioned radially of said rotating electrode.

10. The method according to claim 2 wherein the angles formed between the longitudinal axes of the electrodes are each about 90°.

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