

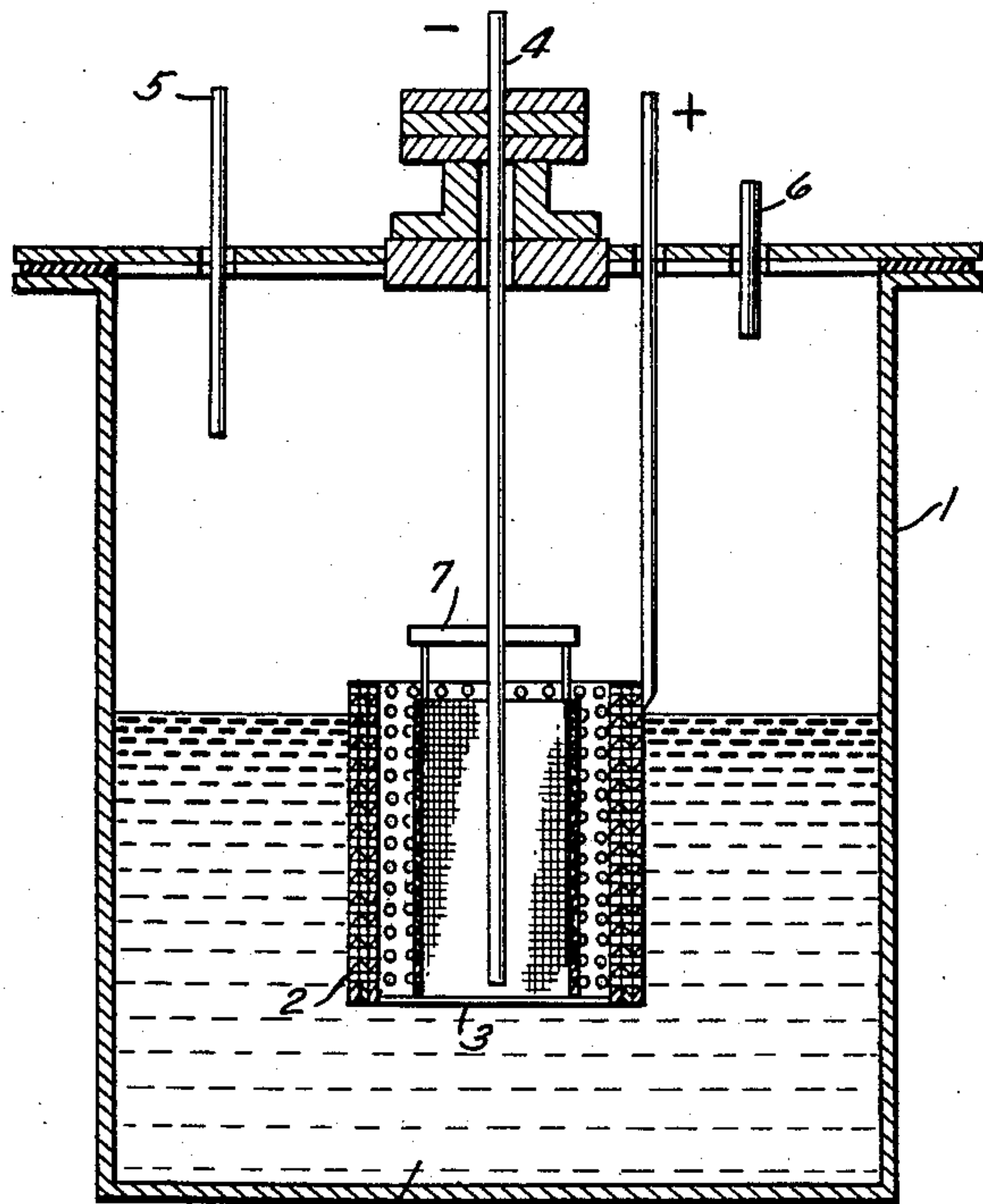
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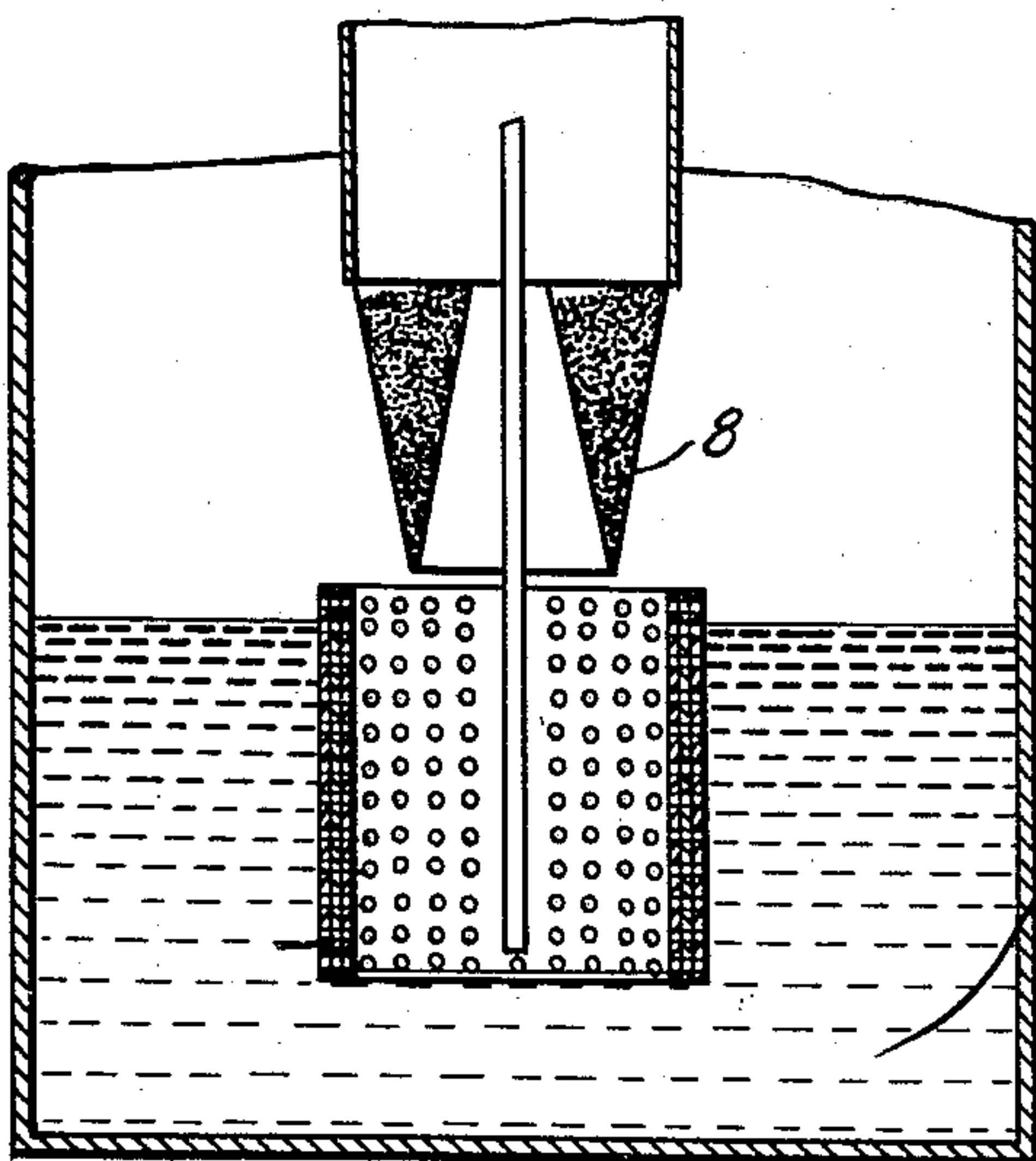
REFINING TITANIUM-VANADIUM ALLOYS

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*Molten Electrolyte*

*Fig. 1*



*Fig. 2*

*Molten Electrolyte*

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REFINING TITANIUM-VANADIUM ALLOYS

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1 Claim. (Cl. 204—64)

This invention relates to the preparation of pure titanium or pure titanium-aluminum alloys and substantially oxygen-free titanium-vanadium alloys made from titanium-vanadium alloys of commercial purity.

Such high purity alloys may be produced by the combination of highly pure metals under especially controlled conditions to prevent contamination during melting, sintering or fabrication. Such highly pure metals are not readily available, and it is therefore advantageous to produce the substantially oxygen-free alloys of my invention by the initial production of alloys from the readily available oxygen-containing materials. It should be understood that the alloys to which I refer as substantially oxygen-free are those containing not more than .05% oxygen and generally in the range .01-.02% oxygen.

The oxygen content of the alloys of my invention may be determined by vacuum fusion, but I prefer to use the method of electrode potential measurement as set forth in my copending application, Serial No. 655,834, filed April 29, 1957, now abandoned.

In the practice of this invention, I utilize the salt bath of my copending application, Serial No. 573,336, filed March 23, 1956, now Patent No. 2,817,631, as an electrolyte. The preferred bath for the practice of my present invention consists of sodium chloride and dissolved therein 5% titanium as lower chloride with an average valence of 2.4 and a dissolved sodium content of 2%.

I have found, however, that good results can be obtained with as low as 1% dissolved titanium as lower titanium chloride having an average valence of 2.05-2.8 and dissolved sodium from .1-4%. The relationship between these constituents is by no means haphazard. The following table shows the general relationship between these parameters:

Table

Percent Ti	Average Valence	Percent Na <sup>o</sup> (in solution)
3.05	2.28	0.28
3.80	2.41	0.32
4.40	2.48	0.70
4.80	2.50	0.94
5.50	2.53	1.36
6.10	2.60	1.42
6.85	2.65	2.24

I have found that the bath may consist of alkali or alkaline earth halides other than sodium chloride. It may, for example, consist of 65% SrCl<sub>2</sub> 35% NaCl; for best results, however, such a bath should contain 8% dissolved titanium as lower chloride with an average valence of 2.4 and containing 6% dissolved alkali or alkaline earth metal.

The procedure for determining alkali or alkaline earth metal and titanium valence in these baths is set forth in a paper entitled "The Chemistry of the Reduction of Titanium Chlorides in Fused Alkaline Chlorides by Solutions of Alkaline Metals" by R. S. Dean, L. D. Res-

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nick and I. Hornstein, Industrial Laboratories, Chicago, Ill., June 1957.

In carrying out my invention, I comminute the initial alloys by any suitable method and make such comminuted alloy an anode in an electrolytic cell having the cell bath described. I place in the cell an inert cathode. The cell arrangement and general parameters of operation are those described in my copending applications.

This particular application to the present invention will be set forth in the examples.

My present invention does not reside in the bath, the cell arrangement or the general method of operation. These are the same as I have previously disclosed for titanium alloy refining.

My invention consists in the steps of alloying titanium in a prescribed manner to obtain the desired anode, passing a direct current from said anode to an inert cathode to obtain a substantially oxygen-free alloy of titanium with the desired composition of alloying.

My invention also encompasses the insertion of a foraminous conducting diaphragm between anode and cathode to intercept the passage of certain metals from anode to cathode and forming thereon certain substantially oxygen-free alloys within the scope of my invention.

I have found that the anodic solution of vanadium from titanium alloys depends not only on their vanadium content but on the content of certain other elements in the anodic material. The most important of these other elements are aluminum and oxygen. The anodic solution of vanadium is hindered by aluminum and favored by oxygen. In the presence of small oxygen contents e.g., .1-.2%, 5% aluminum tends to inhibit vanadium solution from the anodic material. Aluminum, however, dissolves to the extent of about .8% of the titanium dissolved.

The effect of aluminum up to 6% is overcome by the presence of 3% oxygen so that vanadium, but not aluminum, is anodically dissolved. In either case, the cathode produce is substantially free from oxygen.

In the preferred embodiment of my invention, I make an alloy of titanium containing 1% vanadium and 3% oxygen and such amounts of aluminum, iron, nitrogen and carbon as may be incidentally present. I comminute this alloy and use it as anode material. Titanium and vanadium are dissolved from the anode material in about the proportions present. The other elements present in the anode material do not dissolve.

The titanium and vanadium diffuse as chlorides from the anode toward the cathode.

My invention consists in providing a layer of pure titanium in the diffusion path. This may be done in several ways. The simplest and preferred method is to place an iron mesh between anode and cathode. Titanium metal is deposited on this mesh due to its position in the bath when current is passed. This titanium metal removes vanadium from the bath substantially quantitatively.

When the process of my invention is carried out in this way, an alloy of titanium with 3% vanadium is deposited on the titanium coated iron mesh in the form of coarse crystal intergrowths, while pure titanium is formed adherent the cathode.

When the anode material contains less oxygen and more aluminum, e.g., 0.5% oxygen, 5% aluminum and 4% vanadium, the solution of vanadium is inhibited and the coarse crystal intergrowths formed on the screen contain 2% vanadium, while those formed on the cathode contain 0.5% aluminum. These intergrowths are substantially oxygen free.

The foraminous divider is merely a means of providing pure titanium in the diffusion path. The removal of va-



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vanadium is chemical not electrochemical. The vanadium may also be prevented from reaching the cathode by providing a falling stream of pure titanium crystals in the diffusion path in place of the foraminous divider. The crystals may be recovered and re-used until they contain as much as 5% vanadium.

Having now described my invention, I will illustrate it by examples.

*Example I*

The operation was carried out in an electrolytic cell such as that described in Figure 1. The cell was made of a covered cylindrical container 1 composed of type 304 stainless steel within which was supported a basket 2 composed of concentrically mounted bands of perforated steel with  $\frac{3}{10}$ " holes spaced on  $\frac{1}{2}$ " centers. Concentrically mounted within the inner annulus of this basket was a screen 3 composed of low carbon steel which had 16 mesh to the square inch and concentrically mounted within the steel screen was a central rod 4 composed of mild steel.

The anode basket was filled with the crushed product of an ingot which was composed of 5% aluminum, 5% vanadium, 3% oxygen and 86% titanium. The individual anode particles were large enough that they would not pass through the perforations in the basket, but did not exceed  $\frac{1}{2}$  cubic inch in volume. An inlet 5 and outlet 6 were provided so as to keep the inside of the container under a flow of inert gas.

The cell bath consisted of 85% by weight of sodium chloride, 13.4% by weight of titanium chloride (4.8% dissolved titanium as lower chloride) in which the average valence of the titanium was 2.5 and .94% of dissolved sodium metal. The bath was maintained at a temperature of 850° C. by means of electric resistance units surrounding the cylindrical cell container.

External connections were made so that the basket filled with the particulate titanium alloy was the anode; the central rod was the cathode and the screen dividing the anode and cathode was insulated from other parts of the cell by means of a porcelain tube 7.

A direct current of 50 amperes was passed through cell so that there was an anode current density of 1 ampere/sq. in. and a cathode current density of 100 amperes/sq. in. At the end of 12 hours, the current was stopped and the salt drained into another container by melting a frozen salt plug at the drain.

A crystalline material which was scraped from the screen had a particle size coarser than 30 meshes to the square inch and a composition of 5% vanadium, .03% O<sub>2</sub>, balance titanium. A crystalline material was scraped from the cathode which had a particle size coarser than 8 mesh and a composition of .02% oxygen, balance titanium.

*Example II*

The method of Example I was repeated except that the comminuted alloy was composed of 5% V, 1.8% Al, 1% oxygen and balance titanium. The cell bath consisted of 95.3% by weight of sodium chloride, 4.6% by weight of titanium chloride (2.0% dissolved titanium as lower chloride) in which having an average valence of the titanium was 2.05, and .1% by weight of dissolved sodium metal.

The resultant screen product was composed of .4% vanadium, .02% O<sub>2</sub>, balance titanium. The product adherent the cathode was composed of .02% O<sub>2</sub>, balance titanium.

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*Example III*

The method of Example I was repeated except that the current density on the anode was 50 amp./sq. ft. and the current density on the cathode was 5000 amps./sq. ft. A basket hopper containing finely divided titanium 8 as shown in Figure 2 was suspended over the screen area and the screen was not used. By agitating the hopper, a falling stream of finely divided titanium was caused to pass through the electrolyte in the approximate area that was previously occupied by the screen. The resultant cathode product had a composition of .04 O<sub>2</sub>, balance titanium.

*Example IV*

I proceed as in Example I except that I use an anode material which is composed of 5% vanadium, 4% aluminum and 1.5% O<sub>2</sub>.

The resultant product scraped from the screen had a composition of 2% vanadium, 2.2% aluminum and .03% oxygen. The product removed from the cathode had a composition of 1.0% aluminum, .02% oxygen, balance titanium.

*Example V*

In this example I proceed as in Example IV except that I carry out several consecutive runs adding more of the same anode material but using the same bath. Under these conditions the aluminum chloride content of the bath increases. When the aluminum chloride content of the bath increases to more than that corresponding to 1% aluminum, the material deposited at the cathode becomes finely divided, and I prefer to reduce this aluminum content. In the present example I place the bath under a reduced pressure of 5 mm. of mercury for a period of 30 minutes during electrolysis at 850° C. Aluminum chloride distills off and condenses in the cooler part of the cell from which it is recovered. After this step the bath contains .2% Al as chloride, and is satisfactory for further operation.

What is claimed is:

A process of producing coarse crystal intergrowths of pure titanium containing less than .03% oxygen and a vanadium-titanium alloy containing 0.5–5% vanadium and less than .03% oxygen which consists in providing a comminuted titanium alloy anode containing .5–5% vanadium, 1–3% oxygen, and incidental amounts of iron, tin, nitrogen, carbon, and aluminum, the aluminum-oxygen ratio being not more than 2, an initial bath of at least one alkaline chloride having dissolved therein 1–5% titanium as chloride with an average valence of 2.05–2.8 and .1–4% dissolved alkaline metal and an inert cathode, passing a direct current from anode to cathode at a current density of 100–5000 amperes/sq. ft. on the cathode and 1–50 amperes/sq. ft. on the anode material and disposing a layer of pure titanium crystals between the anode and cathode so that the titanium and vanadium chlorides are thereby passed through it in diffusing from anode to cathode to form titanium-vanadium alloy from the layer of titanium crystals by chemical reaction with the vanadium chloride from the said titanium and form coarse crystal intergrowths of pure titanium adherent to the cathode.

## References Cited in the file of this patent

## UNITED STATES PATENTS

2,789,943 Kittelberger ----- Apr. 23, 1957

## OTHER REFERENCES

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