

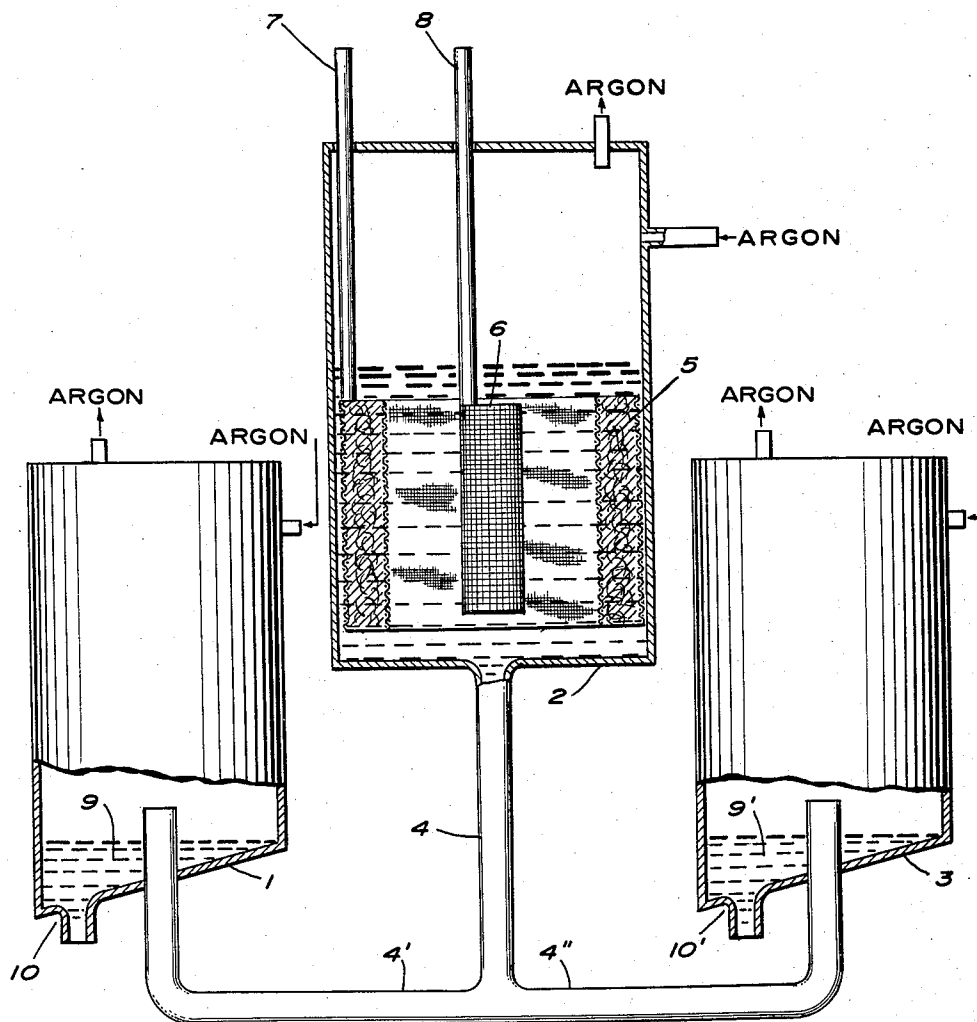
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R. S. DEAN ET AL

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TWO-STEP ELECTROREFINING OF TITANIUM ALLOYS

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INVENTORS

Reginald S. Dean and
William W. Gullett,

BY *Reice, Scheffler & Parker*
ATTORNEYS

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TWO-STEP ELECTROREFINING OF TITANIUM ALLOYS

Reginald S. Dean, Hyattsville, and William W. Gullett, College Park, Md., assignors to Chicago Development Corporation, Riverdale, Md., a corporation of Delaware

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1 Claim. (Cl. 204-64)

This invention relates to electro-refining of titanium alloys containing manganese and/or vanadium and/or chromium.

In our co-pending application, Serial No. 629,298, filed December 19, 1956, we have disclosed that at temperatures above the eutectoid temperature for titanium-manganese, namely, 550° C., manganese behaves in an anomalous manner from an electrorefining standpoint, whereas it dissolves from the anode along with titanium, thus indicating the same, or less, nobility it deposits on the cathode preferentially. It thus appears that manganese is more noble than pure titanium, but less noble than the matrix in impure titanium alloys containing oxygen.

We have found that in the absence of oxygen, titanium manganese, titanium-vanadium, and titanium-chromium alloys can be electrorefined with the manganese (or other alloying metal) remaining in the anode residue. The refining above the eutectoid temperature of titanium alloys containing oxygen in interstitial solid solution and manganese, vanadium or chromium must therefore be carried out in two stages. In the first stage, refining is carried out at an anode current density where titanium and the alloying metal dissolve leaving oxygen in the anode residue. In the second stage, the oxygen free titanium alloy is made the anode and refined at a somewhat lower anode current density. The result of this double refining is the production of highly pure titanium.

This double refining may be done in two entirely separate operations or more conveniently may be carried out in a suitable cell by changing the direction of the current, after effecting the first stage, without removing the cathode product of the first stage from the cell.

Having now described our invention in its most general aspects, we will illustrate it by several examples:

Example I

In this example, we take impure titanium-manganese alloy having a composition, Mn 7.6%, O₂ .21%, N₂ .004%, Fe .15%, balance substantially titanium; the nitrogen and oxygen in this alloy are in interstitial solid solution. We comminute this alloy so as to obtain about 100 sq. ft. of surface per pound. We use a cell such as that illustrated in the figure. The apparatus illustrated in this figure consists of three identical cylindrical steel cells, 1, 2 and 3, connected by a pipe system comprising a pipe 4 leading from the bottom of cell 2 and terminating in branch pipes 4' and 4'' leading to the lower portions of cells 1 and 3, respectively. The anode material is held in an annular steel basket 5; a cathode, illustrated at 6 in cell 2, consists of a cylinder of steel mesh. The anode and cathode are connected to the source of direct current by suitable rods passing through the cell tops and suitably insulated therefrom, illustrated at 7 and 8 in cell 2. The cells are tight and provided with an argon atmosphere. Cell 2 is filled with molten electrolyte so as to immerse anode and cathode, and the pipe system is substantially filled with the electrolyte in solid form.

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When electrolysis is complete, the electrolyte is forced from one cell to one of the other by applying argon pressure and heating the connecting pipe. In this example, we use an electrolyte having a composition as determined in the manner described in co-pending application of R. S. Dean and L. D. Resnick, Serial No. 605,231, filed August 20, 1956, titanium as chloride 5.0%, average valence 2.2, sodium metal as shown by H₂ evolution in acidified ferric sulphate 6.0 ml./gram, balance NaCl. We carry out the electrolysis at 850° C. At the start of the operation of the example we place 5 lbs. of the comminuted anode material heretofore described in the basket 5 and pass 150 amperes D.C. through the cell for 20 hours. The current density on the initial cathode is 600 amperes/sq. ft. At the end of 20 hours about 1500 grams of coarse crystalline metal is adherent the cathode. This analyzes as follows:

	Percent
O ₂ -----	.02
Mn -----	7.8
Fe -----	.02
N ₂ -----	.001

balance substantially titanium.

We now allow the molten bath to flow into cell 1 by heating the connecting pipe system from cell 2 to cell 1. Meanwhile, we have partially filled cell 3 with the initial electrolyte. We now force this electrolyte from cell 3 into cell 2 by heating the pipe system connecting cells 3 and 2, and applying argon pressure. We now connect the crystalline deposit on the wire mesh 6 as the anode and the basket 5 as the cathode and electrolyze as before by passing 75 amperes for 40 hours. This provides a slightly lower anode current density than in the first step, and less than 1/2 the cathode current density used in the first step. We then drain the electrolyte back into cell 3 and allow cell 2 to cool. On removing the basket from the cell, we find that coarse crystals have been deposited on the outside of it. These can be readily removed mechanically and after washing with very dilute acid we obtain about 1350 grams of titanium crystals analyzing, Mn .001%, O₂ .01%, N₂ .001%, Fe .01%, balance substantially titanium. We now add new anode material to the basket, clean off the mesh cylinder 6, close the cell and wash out with argon, then force the original salt bath from cell 1 back into cell 2 and proceed as before.

It will be understood that in the first electrolytic step some manganese chloride accumulates in the salt bath having titanium as chloride 5.0%, average valence 2.2, sodium metal as shown by H₂ evolution in acidified ferric sulphate 6.0 ml./gram, and .03% Mn as chloride, balance NaCl. Consequently, a separate manganese free salt bath having titanium as chloride 5.0%, average valence 2.2, sodium metal as shown by H₂ evolution in acidified ferric sulphate 6.0 ml./gram, balance NaCl must be used in the second electrolytic step. The anode residue from the electrolytic steps either remains inside the basket in the first step or adherent the steel mesh electrode in the second step, or any anode residue falling to the bottom of cell 2 during either electrolytic step is carried in to either cell 1 or cell 3, both of which are provided with sumps 9, 9¹, and outlets 10, 10¹ as shown.

Example II

In this example, we proceed as in Example I, except that after the first electrolytic step we drain the electrolyte into cell 3 and allow cell 2 to cool. We recover the large crystals from the mesh cathode and add new anode material to the basket. We now refill the cell with the same electrolyte from cell 3 and proceed as before. This procedure is repeated until a substantial quantity of cath-

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ode crystals is obtained. These are washed with dilute acid and dried. They are then made the anode material and refined, at a slightly lower anode current density, e.g., .1 ampere/sq. ft., than in the initial refining procedure, in an electrolyte of initial composition maintained in cell 1, the manganese free titanium crystals being recovered from the cathode after each run. The product after dilute acid washing analyzes, Mn .001%, O₂ .01%, N₂ .001%, Fe .02%, balance substantially titanium.

Example III

In this example, we refine an alloy having the composition V 3.2%, O₂ .35%, N₂ .02%, Fe 1.0%, balance substantially titanium. We comminute this alloy so as to obtain 1000 sq. ft. per lb. We use a cell like that in the figure. The electrolyte consists of 65% SrCl₂, 35% NaCl to which has been added titanium chlorides and sodium to produce an analysis of 7% total soluble titanium, and titanium as TiCl₂ of 8.6% by the method of Final Report ONR Contract Nonr 266(24) and a content of dissolved alkaline metal corresponding to 4 ml. of H₂/gram of ferric chloride. This electrolyte is subjected to a preliminary electrolysis in the cell of the figure in which finely divided pure titanium sponge is placed in the basket and 1 ampere passed for 40 hours. The remaining titanium sponge was then removed from the basket and 5 lbs. of the comminuted alloy to be refined placed therein. The electrolyte now analyzed; total soluble titanium 9%, and titanium as TiCl₂ (by the method of Final Report ONR Contract Nonr 266(24)) 14.8%, and 16.2 ml. of H₂ evolved per gram in ferric chloride.

The first stage electrolysis was carried on at 750° C. and 150 amperes D.C. for 20 hours. The current density on the initial cathode was 600 amperes/sq. ft. At the end of this step about 1500 grams of coarse crystalline metal is adherent to the cathode. This analyzes as follows:

	Percent
O ₂ -----	.02
V -----	3.0
Fe -----	.01
N ₂ -----	.001
Sr -----	0.2
Balance substantially titanium.	

We now reverse the terminals and pass 50 amperes D.C. for 55 hours at a cathode current density of about 200 amperes per square ft. based on the initial cathode area. Crystals of pure titanium are built up on the outside of the original anode basket, and a residue containing essentially vanadium with some titanium remains on the original cathode now being used as anode.

The pure titanium crystals on the basket analyze:

	Percent
O ₂ -----	.01
V -----	.001
Fe -----	.001
N ₂ -----	.001
Sr -----	0.2

balance substantially titanium. We wash these with

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dilute acid to remove salt and strontium. The washed crystals contain only traces of impurities and when melted in argon provide a button having a Brinell hardness of 60.

It will be noted that in this example, the same electrolyte is used in first and second steps. This is possible because unlike manganese, vanadium contaminates the bath, but insignificantly.

Example IV

In this example, we refine an alloy having the composition Cr 2.5%, Fe 1.5%, O₂ 0.5%, N₂ .02%, balance substantially titanium. We comminute this alloy so as to obtain 1000 square feet of surface per lb. We then proceed exactly as in Example I. The product of the first electrolysis analyzed:

	Percent
O ₂ -----	.01
Cr -----	2.5
Fe -----	.01
N ₂ -----	.001

balance substantially titanium.

The final product after melting in argon had a Brinell hardness of 60 and analyzed:

	Percent
O ₂ -----	.01
Cr -----	.001
Fe -----	.005
N ₂ -----	.001

balance substantially titanium.

What is claimed is:

In a process of electrorefining an impure titanium containing a substantial amount of oxygen in interstitial solid solution and a substantial amount of manganese alloyed therewith involving the steps of comminuting the oxygen-containing titanium-manganese alloy, making the same an initial anode in an electrolyte consisting essentially of a fused alkaline metal chloride having dissolved therein at least one alkaline metal and lower chloride of titanium, and passing a direct current through the electrolyte from said initial anode to a conductive inert cathode whereby to form an initial cathode product consisting essentially of crystals of substantially oxygen-free metal, the improvement which consists in making said initial cathode product the final anode of a re-refining operation, passing direct current through an electrolyte substantially identical with that of the first refining operation from said final anode to an inert final cathode at an anode current density lower than that employed in the first refining operation and less than 0.3 ampere per square foot to form a final cathode product consisting essentially of crystals of pure titanium and to leave an anode residue containing substantially all of the manganese of said final anode.

References Cited in the file of this patent

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