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PRODUCTION OF TITANIUM AND ZIRCONIUM BY THE ELECTROLYTIC REFINING OF THEIR ALLOYS

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It has already been proposed to refine electrolytically highly contaminated titanium and zirconium metals which could not be used commercially in that condition because of the excessive content of impurities. The metals intended to be processed in that way generally contained oxygen and nitrogen as main impurities. These metals were used as anodes in a molten bath composed of alkaline or alkaline earth metal halides and containing a small proportion of halides of the metal to be purified.

The present invention, which is based on the researches of the applicants, has for its object the direct extraction of titanium or zirconium from alloys of these metals by electrolytic refining.

A preferred form of the invention consists in extracting titanium from ferro-titanium or ferro-silicon-titanium alloys by using these alloys as anodes in a molten bath of alkali halides containing titanium in the form of chlorides—preferably as $TiCl_2$—and using a voltage not in excess of two volts. In this way, there is obtained at the cathode a deposit of titanium substantially free of iron and silicon.

The process can be carried out in the same way by starting with the corresponding zirconium alloys.

In order to obtain a very pure metal at the cathode, it is advisable to select for the anode an alloy which does not contain, or contains only a very small amount of metals capable of forming a solid solution with the metal to be obtained. In the case of titanium, it is advisable to avoid the presence of aluminum and vanadium.

It is also preferable that the anodic alloy contain but small proportions of manganese and chromium.

The anodic alloy can be crushed into lumps of the size of walnuts or hazelnuts which are placed in a metal basket. Some titanium or zirconium chips can also be added and, by their presence in the bath, keep the chloride of the metal to be refined in the subchloride state.

In order to obtain a selective attack on the alloy forming the anode, it is preferable to adopt a moderate anodic current density, for example, less than 100 amperes per kilogram of alloy. Since the anode is constituted of the alloy in comminuted form placed in a basket, it is practically impossible to determine its exact surface. For this reason, the current density has been defined in terms of amperes per kilogram of anodic alloy.

It has been established that the alloy to be refined, which is used as anode in a bath of molten metal chlorides, is not directly attacked by the chlorine ions derived from the titanium or zirconium subchlorides dissolved in the electrolytic bath. These chlorine ions transform the titanium or zirconium subchloride into the tetrachloride, and it is this tetrachloride which dissolves selectively the titanium or zirconium out of the anodic alloy, while being itself converted into subchlorides which are soluble in the bath.

It has also been established that not all titanium or zirconium alloys are capable of being refined under actual commercial conditions, because the solution of the titanium or zirconium out of the anodic alloy sometimes proceeds too slowly or incompletely. Accordingly, a procedure which forms a part of the present invention consists in submitting the alloy to be refined to a blank test by reacting $TiCl_4$, or $ZrCl_4$, with this alloy which is placed in the bath of molten chlorides, for example, at a temperature of 750–800° C., but in the absence of any electric current. Thereupon, the bath is analyzed to determine the proportion of titanium or zirconium subchlorides contained therein, which permits calculation of the efficiency of the dissolution of the alloy.

Alloys having a solution efficiency which reaches or exceeds 75% can be refined under good conditions.

In this way, it has been established that the alloys to be refined should contain at least 65% and, preferably, 70% or more of titanium or zirconium.

It has likewise been established that it is preferable to use for the refining operation those titanium or zirconium alloys the oxide plus nitride content of which does not exceed 8%.

The following examples, which are not given by way of limitation, relate to alloys which fulfill the precise requirements stated above. These examples describe the refining of titanium alloys. Zirconium base alloys are processed in the same manner.

Example 1.—Refining of Fe-Ti

1 kg. ferro-titanium alloy, containing 72.5% Ti and 19.9% Fe, was crushed to walnut and hazelnut sizes and placed in a perforated iron basket, which was then introduced into a NaCl bath kept under an atmosphere of a suitable inert gas. $TiCl_4$ (which had been partially reduced to $TiCl_2$ by the ferro-titanium) was injected into the bath until the titanium content of the bath reached 3.90%. The bath thus prepared was then submitted to electrolysis using the basket as the anode and, on passing current of 55 amperes at a voltage of 1 to 1.5 v. with a counterelectromotive force of 0.1 to 0.3 v., there was obtained at the cathode a crystalline titanium deposit.

Altogether, 410 g. titanium were deposited.

A residue weighing 250 g. was removed from the basket; the Fe-Ti lumps had kept their shape but had become extremely friable. They contained 9.9% Ti and 59.4% Fe. The rest of the titanium was found in the slimes on the bottom of the cell.

The titanium that had been deposited contained 0.025% Fe.

Example 2.—Refining of Ti-Si

A titanium-silicon alloy comprising 72% Ti, 11% Fe and 11% Si, was electrolyzed in a molten bath containing 2.75% Ti as $TiCl_2$. After washing, the obtained cathodic deposit assayed 0.05% Fe and 0.09% Si.

It was proven that the Ti content of the bath did not change during the electrolysis.

When the electrolysis was stopped, it was observed that the anode was surrounded by a porous layer and that the titanium content of the anode had dropped to 59.65%, while that of the Si had risen to 18.35%.

It is also possible to submit to the electrolytic refining process of the present invention alloys rich in titanium but containing various additional elements as, for example, aluminum, chromium, vanadium or manganese. In such cases, the content of the additional elements in the cathodic titanium or zirconium deposit varies greatly depending on the procedure adopted, permitting thereby considerable flexibility shown by the following examples relating to titanium alloys, which do not limit the invention in any way.

Example 3.—Refining of Al–Ti

The commercial Al–Ti alloy having a 70% Ti content is used as the soluble anode in a molten bath containing about 5% titanium in the form of subhalides. The electrolysis is effected with an interpolar distance large enough to require 5 v. when an 80 amperes current is passed through the cell, the counter-electromotive force being of the order of only 0.6 v. Titanium crystals containing 1 to 5% Al are collected at the cathode.

Example 4

The anodic alloy is TiCrFe containing 2.7% chromium and 1.3% iron.

The anode is constituted of 4 kilos scrap alloy. An average current of 30 amperes at a voltage of the order of 1 volt is passed through a molten bath at 750° C.

At the beginning of the electrolysis, there is obtained at the cathode titanium metal having a Brinell hardness of less than 150 and containing 0.07% iron and 0.01% chromium; this result continues until the

$$\frac{\text{deposited Ti}}{\text{charged Ti}}$$

ratio attains the value of about 27%.

If the electrolysis is continued without the addition of any fresh alloy, the iron content of the deposited titanium does not change but the chromium content increases to 0.024% until the

$$\frac{\text{deposited Ti}}{\text{charged Ti}}$$

ratio reaches 40%.

Beyond this point, the iron and chromium increase simultaneously. But, if fresh alloy be added at the point when 27% of the initial titanium has been converted to refined titanium, then, titanium metal containing little iron and very little chromium will continue to be obtained at the cathode. The addition of fresh alloy can be repeated a large number of times without altering this result.

When a slightly higher chromium content can be tolerated in the cathodic titanium, then, fresh alloy should only be added at the time when the

$$\frac{\text{deposited Ti}}{\text{charged Ti}}$$

ratio reaches 40%.

If fresh alloy is not added, then, it is possible to separate successively different cathodic deposits having progressively increasing iron and chromium contents but which are free of oxides and nitrides, and which can, for example, be remelted in the absence of air to reform an alloy of the same composition as the initial alloy but of a higher quality. The anodic residue, which is discarded, contains under the conditions much higher proportions of iron and chromium than in the initial alloy.

Example 5

The anodic alloy is a titanium alloy containing 4% aluminum and 4% vanadium.

The conditions of the electrolysis are the same as in Example 4.

By continuing the electrolysis until about 22% of the charged titanium has passed into the cathodic deposit, there is obtained titanium metal having a Brinell hardness less than 120 and containing 0.02% Fe, 0.02 to 0.10% Al and 0.18 to 0.45% V.

For a ratio of

$$\frac{\text{deposited Ti}}{\text{charged Ti}}$$

greater than 22% and less than 50%, the resulting deposits are richer in Al and V but are free of oxides and nitrides, and when remelted in the absence of air, they

permit the reconstitution of Ti, 4% Al, 4% V alloy of good quality.

Of course, fresh alloy can be added during the refining process as has been indicated in Example 4.

Example 6

The anodic alloy is a titanium alloy containing 4% manganese and 4% aluminum.

The electrolysis conditions are the same as in Examples 4 and 5.

Manganese separates at the cathode as soon as the electrolysis begins.

Up to a

$$\frac{\text{deposited Ti}}{\text{charged Ti}}$$

ratio equal to 53% there is produced an alloy at the cathode with the following composition:

Fe=0.02% Al=0.2% Mn=7.5 to 3.8%

that is to say, a manganese titanium alloy containing very little aluminum. If the electrolysis be continued without adding fresh alloy, the manganese content of the cathodic deposit decreases to 1.5–2% and the aluminum content increases to 13–15%. However, if fresh alloy be added periodically before the

$$\frac{\text{deposited Ti}}{\text{charged Ti}}$$

ratio amounts to 50%, a low aluminum titanium-manganese alloy will continue to be produced at the cathode.

Results of the same order can be obtained when zirconium alloys are used as the anodic alloys.

Generally stated, in the process of this invention, fresh anodic alloy is added to the cell when the quantity of the desired metal deposited amounts to 20–50% of the content of the desired metal in the anodic alloy.

A molten bath of NaCl was used in the several examples given above; however, it is to be understood that other molten halides, such as bromides, iodides and fluorides can likewise be used; also mixtures of various halides. Similarly, halides of other alkali and alkaline earth metals can be used, especially those of potassium, strontium, calcium, barium, and lithium. Mixtures of halides—especially chlorides—of several alkali and alkaline earth metals are suitable for the purposes of this invention. Magnesium halides can likewise be used effectively for the purposes of the present invention and in the appended claims are included in the expression "halides of the alkaline earth metals."

The cathode used in the examples was formed of iron; however, any other suitable material, such as nickel, can be used.

We claim:

1. A process for producing electrolytically a desired metal selected from the group consisting of titanium and zirconium from alloys thereof comprising at least one of the metals selected from the group consisting of Fe, Si, Al, Cr, V and Mn, and containing between 65% and 96% of the desired metal, comprising the steps of forming in an electrolytic cell, containing an anode comprising said alloy of the desired metal and a cathode, a molten bath consisting essentially of at least one halide of a metal selected from the group consisting of the alkali and alkaline earth metals; introducing into said bath a subhalide of the desired metal; passing electric current through said bath whereby the desired metal is selectively dissolved out of the anode and deposited on the cathode; and adding fresh anodic alloy to the cell when the quantity of the metal deposited amounts to 20–50% of the content of the desired metal in the anodic alloy.

2. Process according to claim 1, wherein the molten bath contains NaCl and the subhalide is the dichloride of the desired metal.

3. Process according to claim 1, wherein the sum of the oxide and nitride impurities of the anodic alloy does not exceed 8% by weight.

4. Process according to claim 1 wherein the anodic alloy is ferro-titanium.

5. Process according to claim 1 wherein the anodic alloy is ferro-silicon-titanium.

6. Process according to claim 1 wherein a minor quantity of the desired metal is added to the bath whereby the presence of the subhalide of the desired metal in the bath is enhanced.

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