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REMOVAL OF OXYGEN FROM METALS

Bertram C. Raynes and Merle E. Sibert, Euclid, Ohio, assignors, by mesne assignments, to Horizons Titanium Corporation, Princeton, N. J., a corporation of New Jersey

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This invention relates to the purification of certain metals and, more particularly, to the removal of oxygen present as an impurity in certain metals having a pronounced affinity for oxygen.

There are a number of metals which not only have a great affinity for oxygen but which are extremely sensitive to the presence of small amounts of oxygen in the form of an impurity in the metal. Titanium is illustrative of such a metal. For example, the presence of as little as 0.5% by weight of oxygen in otherwise pure titanium metal will produce a threefold increase in the hardness of the metal, an increase so great as to render the metal unworkable on a commercial scale. In the case of titanium and zirconium, the presently available methods for producing these metals tend to yield the metal in ingot form with a larger percentage of contained oxygen than is compatible with optimum mechanical properties for the metal. To the best of our present knowledge, there is no available procedure for removing this contained oxygen from titanium metal, although its oxygen content can be lowered somewhat by blending the oxygen-containing titanium with substantially oxygen-free titanium.

We have now discovered that it is possible to remove by electrolytic means at least a major portion of the oxygen content of metals of the type in which oxygen dissolves interstitially. More specifically, we have found that when these oxygen-containing metals are made anodic in an electrolytic cell and when the anode voltage is sufficiently low to prevent anodic oxidation of the metal, the oxygen component of the metal can be caused to be transported through the bath and be deposited on the cathode. This discovery is applicable, we have found, to the removal of oxygen from titanium and zirconium. The method of our invention for removing oxygen from these metals comprises anodically electrolyzing the oxygen-containing metal at a voltage below that at which the anodic metal is electrolytically oxidized in an electrolyte containing carrier ions of the metals, continuing the electrolysis until a substantial portion of the oxygen content of the anodic metal has been transported to the cathode, and has thereby been removed from the anodic metal, and recovering the resulting deoxidized anodic metal.

The electrolytes in which the deoxidation of the aforementioned metals is effected pursuant to our invention may be a fused salt electrolyte. The electrolyte should contain carrier ions of the metal which is to be deoxidized by the method of the invention. For example, useful fused salt baths may be made up of alkali metal halides or alkaline earth metal halides or mixtures of such halides. The choice of metal and halide components for such a bath has no apparent effect upon the operability of our method, the choice of bath components being predicated primarily upon the melting point and volatility of the fused bath. Any of the halides of the metal to be oxidized may be used as the source of carrier ions in the fused salt bath, and these halides may

be the simple halides or the complex halides such as the double fluorides of the metal and an alkali metal.

The cells in which this electrolytic purification may be performed by the practice of our invention comprise any of the conventional cell designs which have been found useful heretofore. When the electrolyte comprises one or more salts maintained in the fused state, the cell should of course be of conventional closed design so as to permit the maintenance of an inert cell atmosphere to prevent contamination of the bath, and hence the metal, with oxygen or nitrogen from atmospheric air or moisture.

The oxygen-containing metal which is to be purified by the method of our invention may be present in the electrolyte in any physical form ranging from finely divided metal to large and coherent masses of the metal. The finely divided metal may be made anodic simply by charging it into the bath and by permitting it to rest on the bottom of the bath container which also serves as the anode for the cell or by maintaining it within the confines of an anodically connected porous barrier surrounding the cell anode. Massive pieces of the oxygen-containing metal may be similarly charged into the bath or may be used directly as the bath anode. Regardless of the form in which the oxygen-containing metal is present in contact with the electrolyte, it must be made anodic by suitable electrical connection. The anode voltage which is used in practicing our invention should be sufficiently low to prevent anodic oxidation of the metal. In general, the anode voltage should be less than about 2 volts and voltages less than about 1 volt are generally satisfactory. It must be understood, however, that the anode voltage limit depends upon the metal itself and upon the electrolyte composition, the only requirement being that the anode voltage is low enough to prevent anodic oxidation of the metal to be purified. Within these prescribed conditions, the oxygen component of the anodic metal is transported through the electrolyte and is deposited on the cathode, generally in the form of a high oxygen-content form of the anodic metal. The metal component of the anodic oxygen-containing metal is largely unaffected by this electrolysis and remains in its original form except for the depletion of its oxygen content. After electrolysis has proceeded for a sufficient period of time to transport a significant proportion of the oxygen component of the anodic metal to the cathode, it will be found that the anodic metal residue comprises high purity metal largely freed of its initial oxygen impurity.

The following examples are illustrative of the practice of our invention:

Example I

A mixture of 4 parts of sodium chloride and ½ part by weight of potassium fluotitanate (K_2TiF_6) was fused in a graphite crucible enclosed in a vessel in which an inert atmosphere of argon was maintained. The graphite crucible served as the anode of an electrolytic cell, the cathode being a graphite electrode inserted into the center of the fused salt bath. About 75 parts by weight of titanium metal containing about 0.5% oxygen by weight and having a Brinell hardness number of 220 were added to the fused salt bath wherein the titanium sank to the bottom and rested in electrical contact with the graphite crucible anode. An electrolyzing voltage of 2 volts was applied across the anode and catohde, and electrolysis was continued at this voltage while maintaining the bath temperature at about 800° C. for a period of one hour. Electrolysis was then discontinued and the bath was allowed to cool in the inert atmosphere. The resulting solidified bath was removed en masse from the crucible and this mass was then separated from the cen-

trally positioned cathode. A small deposit of titanium metal very high in oxygen was deposited on the cathode. Substantially all of the added titanium metal remained in the metallic state and was separated from the solidified bath by grinding and leaching of the salt components. The titanium metal thus recovered from the salt bath was arc melted in an inert atmosphere by conventional procedure. The resulting titanium billet was found to have an oxygen content of about 0.1% and had a Brinell hardness number of about 150.

Example II

Into a bath identical with that described in Example I there were inserted both a graphite cathode and an anode of sintered titanium sponge having an oxygen content of about 0.5% by weight and a Brinell hardness number of about 220. The fused salt bath was maintained at a temperature of about 800° C., and electrolysis was carried out for one hour at 1.5 volts. The titanium anode was then withdrawn from the fused salt bath and was cooled in an argon atmosphere. The oxygen content of the thus-treated titanium metal was found to be about 0.1% and its Brinell hardness number was about 150.

Example III

A mixture of 3 parts of sodium chloride and 1½ parts by weight of potassium fluozirconate (K_2ZrF_6) was melted on a crucible and cell such as that described in Example I. Both of the reagents were substantially oxide-free and were anhydrous. Electrolysis was carried out between a graphite cathode and a tubular zirconium metal anode both inserted in the fused salt bath. The zirconium metal contained about 0.7% by weight of oxygen and had a Brinell hardness number of 210. Electrolysis was continued at a voltage slight less than 2 volts for 90 minutes, and after the electrolysis was terminated the anode was withdrawn from the fused bath and was cooled in an argon atmosphere. The oxygen content of the resulting zirconium metal anode was 0.07% by weight and its Brinnell hardness number was 145.

It will be appreciated, accordingly, that the method of our invention makes it possible to remove by electrolytic means the small oxygen content in the aforementioned transition metals so as to reduce their hardness to the point where they may be fabricated by conventional procedures. Our method thus makes it possible to obtain malleable metal from the oxygen-containing metals produced by various metallurgical and electrolytic procedures which heretofore have been considered limited to the production of relatively hard unworkable metals characterized by a small but significant oxygent content.

We claim:

1. The method of removing oxygen from oxygen-containing metals of the group consisting of titanium and zirconium which comprises anodically electrolyzing said oxygen-containing metal at a cell voltage below about 2 volts in a fused halide salt electrolyte containing carrier ions of said metal, continuing the electrolysis until a substantial portion of the oxygen content of the anodic metal has been transported to the cathode and has thereby been removed from the anodic metal, and recovering the resulting deoxidized anodic metal.

2. The method of removing oxygen from oxygen-containing metals of the group consisting of titanium and zirconium which comprises electrolyzing said oxygen-containing metal as the anode at a voltage below that at which the anodic metal is electrolytically oxidized in a fused electrolyte containing carrier ions of said metal, continuing the electrolysis until a substantial portion of the oxygen content of the anodic metal has been transported to the cathode and has thereby been removed from the anodic metal, and recovering the resulting deoxidized anodic metal.

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