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ELECTROLYSIS OF TITANIUM TETRACHLORIDE TO PRODUCE TITANIUM

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This invention relates to the preparation of metallic titanium by the electrolysis of titanium tetrachloride and more particularly to such electrolyses carried out in a fused salt bath of salts such as sodium chloride, potassium chloride, calcium chloride, magnesium chloride, similar salts, and mixtures of these. The fused salt baths to which the invention applies can be classed specifically as salt baths consisting essentially of at least one chloride salt of the group consisting of alkali metal chlorides and alkaline earth metal chlorides.

Recent advances in the preparation of metallic titanium have shown that it is possible to prepare titanium metal electrolytically, by reduction of titanium tetrachloride in a fused bath of, for example, the aforementioned chloride salts. In order to ensure the desired result, various operating conditions and expedients must usually be observed, since titanium tetrachloride readily reacts with oxygen and/or moisture of the air, and titanium metal readily reacts with oxygen and nitrogen at elevated temperatures; such reactivity favors undesirable side reactions which consume the raw material or product, and reduces the yield and purity of metal.

Among the various operating conditions which it is usually highly desirable to maintain under strict control are the voltage drop across the electrolytic cell in which the electrolysis of titanium tetrachloride is carried out, and the electrolytic current flowing through the cell. These conditions are closely associated, and changes in the voltage drop across the cell cause changes in the amount of current flowing through the cell. Since it is usually desired to keep both these conditions constant, it is doubly important to maintain control over the voltage drop across the cell.

The most serious factor affecting the voltage drop across the cell is the common phenomenon of polarization at the anode, or "anode effect" as it generally known in the art of electrolysis in fused salt media. Anode polarization has been found to occur unpredictably during electrolysis of titanium tetrachloride to metallic titanium in fused salt media, even though the electrolysis is carried out with anode current densities much lower than those commonly used in electrolyses in fused salt media. The nature of "anode effect" is clearly described by Mantell in "Industrial Electrochemistry," 2nd ed., page 395 et seq. During the occurrence of an anode effect, the voltage drop across an electrolytic cell increases greatly and fluctuates out of control, and the current is forced down to a very low and unsteady level. These and other undesirable results caused by polarization are detrimental to the production of metallic titanium in electrolytic cells, and it is therefore desired to reduce or eliminate the polarization or "anode effect" in such cells.

The prior art has taught that anode polarization in fused electrolytes is relieved by agitation of the electrolyte and/or of the anode to break the gas film formed around the anode during polarization. However, such practice is awkward and does not serve readily to prevent polarization; it merely corrects it once it has started. It has also been the practice in the copper industry to degas molten copper by stirring with a green pole, which would cause considerable agitation and release undersirable gas from the molten mass; this practice has been found similarly to relieve anode effect temporarily, but does not prevent further anode effects after stirring is stopped. It has also been a practice to scrape the surface of anodes to break the gas film around them and overcome the polarization. Again the method merely relieves and does not prevent polarization.

In electrolytic cells containing a mixture of fused electrolytes, the constituents have sometimes been found to depolarize each other's cathodic discharge; this may sometimes have served to prevent uncontrolled cathode polarization, but it has not been found to prevent anode polarization during electrolysis of titanium tetrachloride in a mixture of fused salts. Since it is not desired to produce a mixture of products, but rather only pure titanium, this method of controlling polarization is not suitable for the electrolysis of titanium tetrachloride.

Attempts have been made to control polarization by interrupting the direct electrolyzing current, and substituting therefor an alternating current for a period up to fifteen minutes in length. Such periods of alternating current heating have been found to relieve polarization, but not to prevent its recurrence.

Attempts have also been made to control polarization in fused salt electrolytes by addition thereto of such materials as conductive acetylene black, sugar (which chars to carbon), and finely divided metals such as magnesium turnings, titanium sponge, finely divided calcium, etc. These materials have not been found satisfactory to prevent polarization or anode effects during the electrolysis of titanium tetrachloride in fused salt baths.

It has now been found that polarization and anode effects during electrolysis of titanium tetrachloride in fused salt baths can be substantially completely prevented by the presence in the bath of a very small proportion of a fluoride salt, such as, for example, sodium fluoride, potassium fluoride, lithium fluoride, calcium fluoride, potassium titanium fluoride (K_2TiF_6), and sodium alminum fluoride (Na_3AlF_6).

Since polarization or anode effects do not occur under all electrolysis operating conditions, it has not been found necessary always to maintain a specific concentration of single fluoride salt in fused baths in which titanium tetrachloride is being electrolyzed to titanium. However, whenever conditions have been such that polarization has occurred in such electrolyses, it has been found possible to relieve the polarization and prevent its recurrence by addition to the bath of fluoride salt in an amount to provide between about 0.02% to 0.10% combined fluorine, by weight of the fused electrolyte in the bath.

The invention thus comprises, in the electrolysis of titanium tetrachloride in fused salt baths, the method of preventing polarization by maintaining in the fused salt bath a small effective proportion of a fluoride salt. Simple, single fluoride salts have been found effective for purposes of the invention, and double fluoride salts also have been found to be effective. The alkali metal fluorides, for example sodium, potassium, and lithium fluorides, have been found to be most effective, and are therefore preferred, but alkaline earth metal fluoride, for example calcium fluoride, and double fluorides, for example potassium titanium fluoride (K_2TiF_6) and sodium aluminum fluoride or cryolite (Na_3AlF_6) have also been found to be effective.

The proportion of depolarizing fluoride salt in the salt bath is fairly important for purposes of this invention, since it has been found that proportions providing substantially less than 0.02% combined fluorine, e. g. 0.005%, are

often unsatisfactory for preventing or relieving polarization as aforesaid, and also proportions providing substantially more than 0.10%, e. g. 0.15%, are often unsatisfactory for preventing or relieving polarization as aforesaid.

The depolarizing salt can be added to the fused salt bath before electrolysis of titanium tetrachloride, or during electrolysis if, as, or when polarization occurs. The depolarizing salt is slowly consumed or destroyed during electrolysis, and additional depolarizing salt must occasionally be added during the deposition of titanium or between periods of deposition, in order to maintain a proportion of 0.02% to 0.10% combined fluorine in the fused bath and prevent recurrence of polarization.

Example 1

In an electrolytic cell of the type used in the process described in British Patent 678,807 and containing 386 lb. of fused electrolyte consisting of equal weights of sodium chloride and potassium chloride, titanium tetrachloride was electrolyzed to titanium metal by adding the vapors thereof at a uniform rate to a confined space over the electrolyte surrounding the cathode. The fused electrolyte was held at a temperature around 1275° F., and a voltage of about 20 volts applied across the electrodes forced a current of about 800 amperes through the cell. The anode submerged in the molten electrolyte had a surface area of about 250 square inches in contact therewith, while the immersed cathode surface in contact with molten electrolyte was about 120 square inches. Minimum and maximum distances between the electrodes were 8 inches and 12 inches respectively. In a series of three runs, during which quantities of 3.74 kilograms, 4.18 kg., and 5.10 kg. of $TiCl_4$ respectively were added over 5 hour periods, and after each of which metallic titanium was recovered from the fused electrolyte, numerous "anode effects," or polarization periods, occurred; these anode polarization effects caused large increases in the voltage drop across the cell, with potential differences as large as 42 volts being observed. The polarization persisted each time for many minutes, and could not be relieved at will by various expedients known in the prior art. During the next run in the same series, in which 4.50 kg. $TiCl_4$ was added over a 5 hour period, when polarization started to occur and the potential between the anodes started to increase, 200 grams of potassium fluoride was added to the electrolyte. This provided about 0.037%, by weight of the electrolyte, of combined fluorine in the cell. The polarization effect quickly stopped, and the remainder of the run was completed without any recurrence of polarization whatsoever, the voltage remaining constant at 20 volts to the end of the run.

Example 2

In the same electrolytic cell used in Example 1, 360 lb. of fused salt consisting of equal weights of sodium chloride and potassium chloride, were used as electrolyte for the electrolysis of 1.77 kg. of titanium tetrachloride to titanium metal as in the previous example. During electrolysis, with a voltage of around 22.9 volts across the electrodes, a current of about 900 amperes flowed through the cell, while the temperature was held around 1365° F. The $TiCl_4$ was added over a period of 2¼ hours. When polarization at the anode started to occur, 200 grams of sodium fluoride were added to the electrolyte. This provided about 0.056% by weight combined fluorine in the electrolyte. The polarization was stopped completely, and the electrolysis continued at uniform voltage and current.

Example 3

Another series of electrolyses similar to Example 2 was conducted in the same cell used in Example 1, but with suspended anodes immersed in the electrolyte to provide 235 square inches of immersed anode surface and 8 to 12 inches between electrodes, with about 450 pounds of fused salt consisting of equal weights of sodium chloride and potassium chloride as electrolyte, and with about 19.3 volts potential across the cell giving a current of about 885 amperes through the cell at a temperature around 1365° F. Quantities of about 4½ to 5 kg. of $TiCl_4$ were used in each run, the quantity being added over a period of about 5 hours in each case. Portions of sodium fluoride were added to the electrolyte during the successive runs in which the titanium tetrachloride was electrolyzed to metallic titanium. An initial proportion of about 0.1% sodium fluoride in the fused electrolyte prevented polarization at the anode, which had previously been occurring. On increasing the proportion of sodium fluoride in the electrolyte to about 0.3% by weight, polarization again occurred and continued to affect the operations until the proportion of sodium fluoride was reduced.

Example 4

In the same cell used in Example 3, 511 lb. of fused salt were used as electrolyte for the electrolysis of 5.55 kg. of titanium tetrachloride to metallic titanium, the $TiCl_4$ being added uniformly over a period of 3¾ hours. The salt consisted of 17.6% by weight of strontium chloride and 41.2% by weight of each of sodium chloride and potassium chloride. With the salt at a temperature around 1285° F. and 21 volts potential across the cell, a current of 1055 amperes flowed through the cell. When polarization started to occur, 200 grams of sodium fluoride were added to the fused electrolyte, and no further polarization occurred during the run.

Example 5

In another run similar to Example 4 above, a fused salt electrolyte, consisting of 12.8% strontium chloride and 43.6% by weight of each of sodium and potassium chlorides, was used in the electrolysis of 5.77 kg. of titanium tetrachloride to metallic titanium, the $TiCl_4$ being added uniformly over a period of 4½ hours. At a temperature around 1360° F. in the electrolyte, with about 19.2 volts potential across the electrodes, a current of about 920 amperes flowed through the cell. Again on the occurrence of polarization, 200 grams of sodium fluoride were added to the electrolyte, and the polarization was completely arrested and did not recur throughout the run.

Examples 6–9

In other electrolyses similar to the foregoing, polarization has been relieved by addition to the fused electrolyte of the following fluoride salts in quantities to provide the indicated percentage of combined fluorine during electrolysis of titanium tetrachloride to metallic titanium.

Example No.	Salt	Weight Percent Combined F
6	$AlF_3 \cdot 3NaF$ (Cryolite)	0.071
7	LiF	0.070
8	CaF	0.031
9	K_2TiF_6	0.045

It will be understood that the invention is not limited to the specific expedients described in the foregoing examples, but includes all the numerous expedients covered by the scope of the appended claims.

We claim:

1. In the electrolysis of titanium tetrachloride in fused salt baths consisting essentially of at least one chloride salt of the group consisting of alkali metal chlorides and alkaline earth metal chlorides, the method of preventing polarization by maintaining in the fused salt bath a proportion of a fluoride salt to provide between 0.02% and 0.10% by weight of combined fluorine in the fused salt bath.

2. The method as claimed in claim 1, in which the fluoride salt is a single fluoride salt.

3. The method as claimed in claim 2, in which the fluoride salt is an alkali metal fluoride.

4. The method as claimed in claim 3, in which the fluoride salt is sodium fluoride.

5. The method as claimed in claim 1, in which the fluoride salt is a double fluoride salt.

6. The method as claimed in claim 5, in which the fluoride salt is sodium aluminum fluoride.

7. The method as claimed in claim 5, in which the fluoride salt is potassium titanium fluoride.

8. The method as claimed in claim 2, in which the fluoride salt is calcium fluoride.

9. In a process for the production of metallic titanium by the electrolysis of titanium tetrachloride in a fused salt bath consisting essentially of at least one chloride salt of the group consisting of alkali metal chlorides and alkaline earth metal chlorides, the step of conducting the electrolysis in the presence in the bath of a proportion of a fluoride salt of the group consisting of alkali metal fluorides, calcium fluoride, and double fluoride salts, said fluoride salt providing between 0.02% and 0.10% by weight of combined fluoride in the fused salt bath.

10. The step as claimed in claim 9, in which the fluoride salt is an alkali metal fluoride salt.

11. The step as claimed in claim 10, in which the fluoride salt is sodium fluoride.

12. A method for relieving and preventing polarization during electrolysis of titanium tetrachloride to metallic titanium in a fused salt bath consisting essentially of at least one chloride salt of the group consisting of alkali metal chlorides and alkaline earth metal chlorides, comprising adding to the fused salt bath a proportion of a fluoride salt of the group consisting of lithium fluoride, sodium fluoride, potassium fluoride, calcium fluoride, potassium titanium fluoride, and sodium aluminum fluoride, said fluoride salt providing between 0.02% and 0.10% by weight of combined fluorine in the fused salt bath.

13. A method as claimed in claim 12, in which the fluoride salt is sodium fluoride.

14. A method as claimed in claim 12, in which the fluoride salt is potassium fluoride.

15. A method as claimed in claim 12, in which the fused salt bath comprises one or more salts of the group consisting of sodium chloride, potassium chloride, calcium chloride, and magnesium chloride.

16. A method as claimed in claim 15, in which the fluoride salt is added to the fused salt bath before commencement of electrolysis.

17. A method as claimed in claim 15, in which the fluoride salt is added to the fused salt bath on the occurrence of polarization.

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