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PROCESS FOR THE PRODUCTION OF METALLIC NIOBIUM OR TANTALUM BY AN ELECTROLYTIC METHOD

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This invention relates to the production of metallic niobium or tantalum by an electrolytic method, more especially the production of these metals from oxygen-free, that is to say, oxide-free, fluoride-containing melts, by electrolysis.

Copending application Serial No. 677,796, filed August 12, 1957, and now Patent No. 2,956,936, by K. Huber et al., discloses a process for the production of metallic niobium or tantalum by the electrolysis of a melt, in which a double fluoride of niobium and/or of tantalum is electrolysed in a melt of an oxygen-free alkaline earth halide or alkali metal halide. A disadvantage of the process is that the content of the double fluoride decreases during the process in proportion to the separation of metal and becomes replaced by an alkaline earth fluoride or alkali metal fluoride. Since the occurrence of the undesirable so-called anode effect depends on the concentration of such fluoride, the anodic current density must be reduced as the fluoride content increases. In such a process it is therefore not possible to work continuously and at the same time under substantially constant conditions, such as are desirable in the interests of the quality of the metal obtained.

The present invention is based on the observation that a process for the production of metallic niobium or tantalum by the electrolysis of a melt can be carried out under substantially constant conditions by introducing the vapour of the pentachloride of the metal into an oxygen-free melt consisting of an alkaline earth metal chloride and/or alkali metal chloride and an alkaline earth metal fluoride or an alkali fluoride, carrying out the electrolysis at an anodic current density just below the critical value for the anode effect, and continuously introducing the pentachloride vapour into the melt during electrolysis.

It is of advantage to introduce the pentachloride vapour at such a rate into the melt that the concentration of the metal to be produced remains substantially constant in the melt during the electrolysis. The maintenance of a substantially constant concentration of metal in the electrolyte is one of the requirements for producing a final product of uniform quality. Advantageously the pentachloride vapour is introduced at a rate which corresponds stoichiometrically to the effective quantity of current, account being taken of losses in metal yield and current yield.

As the occurrence of the undesirable anode effect in such melts depends on the fluoride content of the melt, the anodic current density is adjusted so as to be just below the critical value for the fluoride content of the melt. This can easily be determined experimentally. The following formula is suitable for making rough calculations, but, of course, it must be borne in mind that the geometrical shape of the cell also has a certain effect. The critical current density depending on the temperature and the fluoride concentration of the melt can be determined empirically from the following formula

$$(1) \qquad \frac{T+5.6(T-750)}{A.e^{0.1A}}+\frac{A}{2.4}\left(1+\frac{T-750}{100}\right)$$

When T is the temperature of the melt in degrees centigrade, e is the Euler number (the base of natural logarithms), and A is the percentage concentration in the melt of fluorine present as "free" fluoride, the result is the critical value for the current density in amperes per square decimetre.

By "free" fluoride is meant the quantity of fluoride present in the melt over and above the combined fluorine calculated in accordance with the following equation:

$$(2) \qquad MeCl_5+\frac{7}{x}A^xF_x=A^x\frac{2}{x}MeF_7+\frac{5}{x}A^xCl_x$$

In Equation 2 Me=niobium or tantalum, and A represents an alkaline metal (x=1) or an alkaline earth metal (x=2). The equation is primarily a formal means for calculating the combined and free fluoride and represents only to a limited extent the true position. Since, as a result of maintaining the metal content of the bath constant by introducing pentachloride vapour, the content of free fluoride remains constant, the critical current density for the anode effect also remains constant during the electrolysis. The process can therefore be carried out at a constant current density and the latter maintained at its maximum value throughout the process.

The lowering of the fluoride content of the melt, which is desired in view of the critical anodic current density, is opposed by the fact that the vapour pressure of the pentachloride above the melt increases as the fluoride content decreases. The said increase is especially pronounced when the quantity of fluoride falls below that required by Equation 2 to bind the pentachloride. It is therefore necessary to work at a fluoride concentration corresponding to the aforesaid quantity of fluoride, as otherwise there will be a considerable loss of the electrolysable compound. Furthermore, as the rate of absorption of pentachloride increases with an increase in the fluoride concentration, it is of advantage to use a concentration exceeding the stoichiometric quantity calculated according to Equation 2. Accordingly, the rate of supply of the metal chloride vapour and the fluoride content of the melt used are advantageously so adjusted relatively to one another that an excess of fluoride of about 10–50% above the fluorine originally present as alkaline earth metal fluoride or alkali metal fluoride is maintained during the electrolysis.

Loss by evaporation in the process at present used is indeed small, as the vapour pressure of the metal chloride issuing from the melt increases with an increase in the concentration of metal, but in the process of this invention, due to the introduction of pentachloride vapour, the whole of the metal compound to be electrolysed is not present in the melt from the outset, but is added continuously during the electrolysis. Thus, the process is operated at a lower concentration of metal and this also reduces loss by evaporation from the melt.

The process of this invention may be carried out, for example, in a cell in which the cathode zone and anode zone are separated from one another. It is of advantage to supply the metal pentachloride vapour directly into the cathode zone. The cathode zone and anode zone may be separated from one another in such way that the chlorine formed at the anode during the electrolysis can flow away without coming into contact with the pentachloride vapour being introduced. In this manner loss of metal due to the entrainment of pentachloride vapour by the chlorine formed at the anode, is avoided. This is all the more the case, when the pentachloride vapour is introduced only into the cathode zone, as then an extremely small concentration of metal exists in the anode zone.

The pentachloride vapour introduced and the chlorine formed during the electrolysis can be separated from one another very satisfactorily by using another form of electrolytic cell. In this cell a cylindrical anode consisting

of graphite is suspended from above and dips into the electrolyte. Within the anode is arranged a rod-like cathode. The anode and cathode are arranged in a vessel containing the electrolyte in which they are immersed. The pentachloride vapour is introduced into the region between the vessel and the outer wall of the anode. The chlorine is formed during the electrolysis solely at the inner surface of the anode cylinder and is led away from this zone in an upward direction without coming into contact with the pentachloride vapour being introduced. In this manner the zone in which vapour is introduced and the anode zone are effectively separated from one another. Between the anode and cathode there may be provided a separating tube, advantageously also of graphite, which serves to protect against chlorine the tantalum tree which is withdrawn from the electrolyte with the cathode, after the electrolysis. In this way any harmful effect of the chlorine on the pentachlorine vapour introduced or on the metal produced is avoided, and losses in yield occasioned thereby are reduced.

It is of advantage so to choose the composition of the melt that it has a low melting point. This can be achieved, for example, by using an equimolecular mixture of potassium chloride and sodium chloride. In other cases it may be of advantage to use an electrolyte having a definite melting point suited to the temperature of the electrolysis. This can be achieved by suitable mixtures of alkaline earth halides and alkali metal halides such, for example, as sodium chloride and barium chloride or the fluorides of these two metals.

It is of advantage to maintain above the melt an inert protective atmosphere free from oxygen. In view of the space available in the cell round the cathode it is necessary, after a certain quantity of metal has been deposited, to remove the cathode from the bath and replace it by a new cathode. "The tree" deposited on the cathode is washed to remove adherent electrolyte therefrom.

In order to reduce the loss of electrolysable metal, which would be lost in the electrolyte washed away, the process may be carried out by stopping the introduction of pentachloride vapour shortly before withdrawing the cathode, and continuing the electrolysis until the metal remaining in the bath has been deposited. The cathode is then withdrawn from the bath. When a fresh cathode is inserted pentachloride vapour is then introduced for a certain period before switching on the current, in order to bring the electrolyte into the state desired for operating the process.

The following examples illustrate the invention, the parts being by weight:

Example 1

There was used as a cell a graphite crucible having an internal diameter of 80 millimeters and a depth of 210 millimeters, which also served as the anode. A nickel rod of 15 millimeters diameter situated in the centre of the crucible dipped into the electrolyte for a distance of about 100 millimeters. In order to separate the anode zone and cathode zone from one another the cathode was surrounded by a graphite tube having a diameter of 60 millimeters and a wall thickness of 3 millimeters. The graphite tube served as a conduit for introducing the pentachloride vapour. The cell was disposed within a quartz crucible which served to exclude the atmosphere and the cell was externally heated electrically.

As the electrolyte in the graphite crucible there was used a melt consisting of 542 grams of NaCl, 398 grams of KCl and 318 grams of KF, and the temperature of the melt was maintained at 750° C. At the beginning of the process tantalum pentachloride vapour was introduced for 50 minutes at a rate of 2.8 grams per minute. The electrolysing current of 60 amperes was then switched on, which gave a voltage between the electrodes of 5.2. During the electrolysis the voltage fell to 4.5.

The introduction of pentachloride vapour was continued at the same rate for 40 minutes, so that a total of 250 grams of tantalum pentachloride vapour was introduced. The introduction of pentachloride was then discontinued and the electrolysis was continued until the voltage had risen to 5.2. Then the bath tension was reduced to 3 volts and the current to 5 amperes. The space above the electrolyte was scavenged with argon, and the tantalum tree deposited on the cathode was withdrawn from the electrolyte. The melt adhering to the metal was washed away with water. There were obtained 96 grams of ductile tantalum powder of medium-fine particle size.

Example 2

In the apparatus described in Example 1 and with the same alkali metal chloride-fluoride melt, a total of 250 grams of niobium pentachloride vapour was introduced for a period of 145 minutes. At a current of 60 amperes the bath tension varied between 4.4 and 4.7 volts. After cutting off the supply of pentachloride, the electrolysis was continued for 25 minutes until the bath tension had increased to 5.2 volts. The electrolysis was then discontinued, and the metal was recovered as described in Example 1. There were obtained 56.3 grams of ductile niobium powder of fine particle size.

Example 3

A melt consisting of 289.2 grams of NaCl, 432.0 grams of KCl and 448.0 grams of BaF_2 was introduced into a cell of the kind described in Example 1. A total of 260 grams of tantalum pentachloride were introduced into the bath and electrolysed at a current of 60 amperes. After stopping the electrolysis and recovering the metal, 82 grams of tantalum powder were obtained.

What is claimed:

1. In a process for the electrolysis of a member selected from the group consisting of niobium pentachloride and tantalum pentachloride in an oxygen-free halide melt comprising a fluoride selected from the class consisting of alkaline earth metal and alkali metal fluorides, wherein the melt is electrolysed at an anodic current density below the critical value for the anode effect, wherein the anodic current density is adjusted in relation to the temperature and fluoride content of the melt so as to be at most equal to

$$\frac{T-5.6(T-750)}{A.e^{0.1A}}+\frac{A}{2.4}\left(1+\frac{T-750}{100}\right)[\text{amp./dm.}^2]$$

in which T is the temperature in degrees centigrade, e is the Euler number, and A is the percentage of fluorine present in the melt, and wherein the pentachloride vapor is continuously introduced into the melt during electrolysis, the step of adjusting the fluoride content of the melt to the quantity of pentachloride introduced so that it is at least equal to the amount required to bind the pentachloride.

2. A process as claimed in claim 1, wherein the fluoride content exceeds the quantity stoichiometrically required to bind the pentachloride.

3. A process as claimed in claim 2, wherein the excess of fluoride amounts to 10–50% of the quantity stoichiometrically required.

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