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(54) Use of treated niobium or tantalum as a connector, such a connector and a cathodic protection system using such a connector.

(57) The use of niobium or tantalum treated in a manner known per se by pickling and anodisation as a connector in a saline solution. Also an electrical connector formed of niobium or tantalum having been treated by pickling and oxidation.

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TITLE MODIFIED
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Use of treated niobium or tantalum as a connector and such a connector

This invention relates to the use of treated niobium or tantalum as a connector and such a connector and has particular reference to the treatment of niobium or tantalum to improve its resistance to a previously unknown crevice corrosion attack.

It has already been proposed to use niobium as a connector, particularly for use in a saline solution such as seawater. Such a connector is described in detail in British published Application No 2 001 807A. Niobium is chosen as a particularly suitable material for such a connector for a number of reasons. The purpose of the connector is to permit a dismantlable connection to be made in an electrical line feeding positive current to an underseas anode in an impressed current cathodic protection system.

The electrical connector proposed in Patent Specification No 2 001 807A has a number of distinct advantages over previous electrical connectors in that it is easily dismantlable and assemblable and by comparison to previous connectors is comparatively inexpensive. Niobium is chosen as a particularly suitable material for such an electrical connector as it is normally recognised that niobium can be connected and operated as an anode in a saline solution, such as seawater, without corroding at anodic voltages less than approximately 100 volts. The anodic properties of niobium are well-known and it is well-known that niobium forms a resistant and insulating niobium oxide film at applied voltages of up to 100 volts. Above that voltage, known as the breakdown voltage, the film fails and the material corrodes rapidly. Before the present invention, however, it was considered that bulk niobium was self-passivating at voltages below the breakdown voltage. Unexpectedly, however, it was found that when connectors formed of niobium were tested they could, in certain conditions, corrode rapidly. Why this should happen was not to be found in any literature known to the applicants. An answer to the problem has now been found and basically the solution, which forms one feature of the present invention, is to pre-treat the niobium by pickling to remove contamination and surface oxide films and subsequently to form an oxide film on the surface of the niobium.

As a result of investigations carried out by the applicants it has been found that such a pre-treatment is known per se but has only been proposed as a method of forming a smooth surface, for example in the treatment of superconductor cavity resonators.

Thus, in British Patent Specification No 1 335 165 there is described the treatment of the internal niobium surface of a superconducting cavity resonator by pickling in a mixture of nitric acid and hydrofluoric acid and subsequently anodising the resonator surface in an aqueous ammonia solution. There is no indication, however, from this prior patent specification that the material so treated is particularly suitable for use as a connector in a saline solution or that such a material would be resistant to corrosion. It is apparent, therefore, that the inventors have discovered an unexpected property of niobium when treated in a manner known per se. The fact that the niobium is, when in use, connected as an anode and yet can suffer from corrosion, increases the novelty of the invention insofar as a pre-treatment comprising pickling and anodisation substantially prevents corrosion at a later date.

It has also been found, as a result of work carried out by the inventors, that pickling alone is not sufficient, nor is anodisation alone sufficient. Thus, it is necessary to have the combination of steps before the beneficial effects of the invention are to be found.

It is, of course, well-known to anodise niobium, as is described, for example, in British Patent Specification No 1 228 939 or US Patent Specification No 3 496 076, and it is also known to pickle and subsequently anodise niobium for use as a superconducting cavity resonator as is described in

British Patent Specification No 1 335 165 referred to above.

It appears that the particular problem associated with the use of niobium as a connector occurs when the niobium is located in a saline solution and is connected anodically. Thus, when niobium is inserted in a cold saline solution but is not connected as an anode it does not corrode. However, when connected as an anode, in certain circumstances it has been found that corrosion can occur. To the best of the inventors' knowledge this fact was never known prior to the making of the present invention.

In US Patent Specification No 3 730 856 there is described a method of anodising titanium or niobium to remove surface ion contamination so as to improve the corrosion resistance of chemical plant where the metal surfaces are in contact with hydrogen. However, there is no reference to the particular advantages to be obtained from using pickled and anodised niobium as a connector in a saline environment.

It has also been proposed - see, for example, British Patent Specification No 1 430 185, to reduce the susceptibility of titanium to crevice corrosion by abrading and pickling in hydrofluoric and nitric acid mixtures to remove ion surface contamination. However, this specification does not point out the advantages of the present treatment of niobium.

In US Patent Specification No 3 876 136 niobium (ie columbium) is used in place of titanium where titanium is said to be susceptible to crevice attack. The specification does not draw the conclusion that pickling and anodisation of the niobium is necessary. In other words, from this specification it will be concluded that niobium is itself resistant to crevice corrosion without the need for any treatment of it.

In US Patent Specification No 3 469 975 it is stated that the problem of containing halide solutions is complicated by the complete unpredictability of susceptibility (of materials) to crevice corrosion. This reference is to be found in column 2, lines 1 to 3, of the specification. In lines 27 to 32 there is further reference to the complete unpredictability of materials to crevice corrosion.

Although crevice corrosion of materials is well-known for materials such as steel - see, for example, a paper published by W D France Jr in a symposium presented at the Seventy-Fourth Annual Meeting of the American Society for Testing and Materials, 27 June to 2 July 1971, published as ASTM Special Technical Publication 516, pages 164 to 196 - there was no indication that niobium was a material which could suffer such a corrosion. Furthermore, in a publication by the Centre Belge d'Etude de la Corrosion published in Brussels, June 1957, reference NZ.55 JVM.144, entitled "Electrochemical Resistance of Niobium" by J Van Muylder, N de Zoubor and M Pourbaix it is stated that the resistance of niobium to corrosion is that of a refractory metal, unattacked in air, oxygen and water, that it is not attacked by normal acids, such as hydrochloric, sulphuric and nitric acids or their mixtures, that aqua regia has no action and that the same is true of caustic alkali solutions. Because it is so inert to reactive chemicals it is necessary to use fused caustic alkalis or alkaline carbides or their complex solutions to attack it.

The paper goes on to say that hydrofluoric acid attacks niobium only slowly but the rate of attack can be increased if the niobium is touched with platinum. Alternatively, the rate of attack can be increased by adding nitric acid to the hydrofluoric acid. It is believed that the niobium forms complex fluorides or oxy-fluorides.

The paper concludes by saying that the known resistance of niobium to the action of chemical agents gives rise to the conclusion that the niobium oxide which forms on the metal constitutes an effective protective oxide. The paper ends by stating that in the absence of complexing substances the metal niobium is virtually non-corrodable.

Thus, contrary to the prior art discussed above, it has been found that the treatment of niobium known per se can give unexpected increases in the resistance of niobium to crevice corrosion, particularly when anodically connected as an electrical connector in a saline solution.

By the present invention there is provided the use of niobium or tantalum, having been treated in a manner known per se by pickling to remove contamination and surface oxide films, and subsequently forming an oxide film on its surface, as a connector in a saline solution. The present invention also provides for the use of niobium in which the oxide is formed by anodisation in a manner known per se. The connector may be used when anodically polarised in the saline solution. The saline solution may be an aqueous saline solution and the niobium may be polarised at a voltage in the range 30-100 volts. The present invention further provides a niobium or tantalum member exposed, in use, to a saline solution and having been treated by pickling to remove contaminated surface oxide films and subsequently having formed on its surface an oxide film.

The present invention further provides a cathodic protection system incorporating such a connector.

By way of example the treatment of niobium and the advantages to be obtained thereby will be described below.

A piece of extruded niobium was partially covered with a piece of plastics tape and was inserted in a hot saline solution and connected as an anode at 50 volts. It was found that after a short period of time white niobium oxide corrosion products were to be found adjacent the piece of plastics tape. Two similar pieces of niobium were then treated in the following manner. A first piece was treated by a method not in accordance with the present invention. It was pickled in a solution of hydrofluoric acid and nitric acid and then washed in water. The material was then again wrapped in tape and connected as an anode at 44 volts in a saline solution containing 250g/l NaCl at a pH of 2. Again, corrosion products were found on the surface.

The second piece of niobium was then pickled in a hydrofluoric acid and nitric acid mixture to remove 40 microns of niobium, washed in water and subseqently anodised in an ammonium sulphate solution at 40 volts to form an anodic film on the surface of the niobium.

This sample was then partially wrapped with a plastics tape and treated in the manner of the first sample mentioned above. This piece of niobium, which had been treated in accordance with the present invention, was found to suffer no attack whatsoever.

By way of comparison third and fourth samples of extruded niobium were merely anodised in aqueous NaCl containing 20g/l and 220g/l NaCl at 40 volts and covered with plastics tape. These samples were then tested in accordance with the first-mentioned sample. This sample, again not in accordance with the present invention, was also found to corrode.

It can thus be seen that the combination of pickling and forming the oxide layer - which could be formed by air oxidation of the niobium - leads to unexpected improvements in the corrosion resistance of niobium when used as a connector, particularly as an electrical connector in a saline solution, such as seawater. It will be realised that hot water was used to accelerate the effect of corrosion. Tantalum behaves in a similar manner to niobium, having a similar normal breakdown potential.

The connectors were particularly useful for cathodic protection installations.

CLAIMS:

1. Use of niobium or tantalum, having been treated in a manner known per se by pickling to remove contamination and surface oxide films and subsequently forming an oxide film on its surface, as a connector in a saline solution.

2. Use of niobium as claimed in Claim 1 in which the oxide is formed by anodisation in a manner known per se.

3. Use of niobium as claimed in Claim 1 or Claim 2 in which the connector is anodically polarised in the saline solution.

4. Use of niobium as claimed in any one of Claims 1 to 3 in which the saline solution is an aqueous saline solution and in which the niobium is anodically polarised at a voltage in the region of 10 to 100 volts.

5. An electrical connector including a niobium or tantalum member exposed, in use, to a saline solution and having been treated by pickling to remove contamination and surface oxide films and subsequently forming an oxide film on its surface.

6. An electrical connector as claimed in Claim 5 in which the oxide film is formed by anodisation.

7. A cathodic protection system incorporating an electrical connector as claimed in Claim 6 or Claim 7.