

Tantalum-Platinum and Titanium-Platinum Bi-Electrodes

ANODIC BEHAVIOUR IN ELECTROLYTES OF LOW CONDUCTIVITY

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Previous studies of the anodic polarisation of titanium in chloride solutions have demonstrated that, when the potential across the oxide exceeds a critical value (12 to 14 volts), film growth ceases owing to breakdown of the oxide film and intense corrosion or pitting occurs at localised areas. Pitting of the titanium can, however, be prevented by having platinum in contact with the metal surface. In these circumstances the entire current will be conducted through the platinum and pitting of the titanium will occur only if the breakdown potential is exceeded. A continuous coating of platinum is not essential, and very high current densities can be applied to a titanium-platinum bi-electrode in sea-water, or other highly conducting electrolytes containing chlorides, without exceeding the breakdown potential (1, 2). The use of platinised titanium as an anode for cathodic protection of structures in sea-water is now firmly established.

The situation is, however, quite different if the electrolyte has a very high electrical resistance as, in these conditions, it is possible to exceed the critical potential with consequent film breakdown and pitting of the exposed titanium. A rod of titanium, coated with platinum over its lower half only, that has been anodically polarised in fresh water (specific conductivity $3 \times 10^2 \mu \text{ mhos/cm}^{-1}$), using a cathode of equal length placed one inch from the anode, at 25 amp/ft² shows appreciable pitting. Owing to the geometry of the system and the very high IR drop through the electrolyte the potential of the

titanium will increase with increasing distance from the platinum and, at a certain point, the breakdown potential will be exceeded. It has been observed, however, that the titanium adjacent to the platinum shows no evidence of pitting. If the experiment had been carried out in sea-water the titanium would have remained unattacked.

Tantalum, unlike titanium, can be anodically polarised in sea-water without the occurrence of pitting, and film growth, as shown by the interference colours, proceeds until the potential is ~ 160 volts, when the film breaks down.

The thick oxide produced in these circumstances is not, however, firmly adherent to the metal and can be readily detached with Sellotape.

The potential of tantalum during anodic polarisation can be demonstrated visually by the brilliant interference colours. If a tantalum-platinum bi-electrode (1 × 1 inch tantalum with platinum, 0.1 × 0.1 inch, welded to the centre) is anodically polarised in sea-water only a first-order blue film will be formed uniformly on the tantalum surface and current will then proceed through the platinum (Fig. 2a). In a low-conductivity water, however, the potential distribution is not uniform and the thickness of the oxide will increase with increasing distance from the platinum microelectrode. This results in a wedge-shaped oxide film (Fig. 2b) which gives rise to five orders of interference as a series of concentric rings around the platinum, as shown in Fig. 1. Since the thickness of

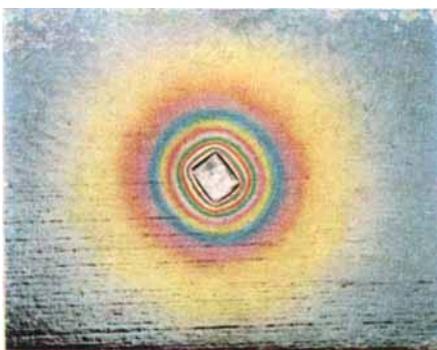


Fig. 1 Interference colours produced on a tantalum-platinum bi-electrode anodically polarised in fresh water. (The first order of interference is immediately adjacent to the platinum and is not revealed in the photograph)

the oxide is a function of the potential (14.5 Å/V for tantalum) it is evident that the potential increases with increasing distance from the platinum.

A similar experiment with a corresponding titanium-platinum bi-electrode resulted in only 1 to 2 orders of interference, as breakdown of the film, at points in the surface where the potential exceeded ~12 volts, precluded further film thickening (Fig. 2c).

Again, however, it is necessary to observe that in no circumstances could pitting be produced in the immediate vicinity of the platinum. Although the potential at which pitting occurs usually corresponds to 12 to 14 volts, this value can be exceeded by careful preparation of the metal surface. Other conditions being equal, a roughly machined surface pits at a lower potential than a surface that has been carefully prepared by polishing or by pre-anodising in a non-corrosive electrolyte.

The bi-electrode previously described represents an extreme case of exposure of titanium to the electrolyte and is unlikely to be encountered in practice. Short-term laboratory experiments have demonstrated that appreciable areas of platinum (0.5 inch diameter) can be removed from platinum-coated titanium without consequent pitting when the metal is used as an anode in a natural fresh water. It would appear from laboratory tests that although platinised tantalum would be preferred, platinised titanium could be used with some confidence as an anode for cathodic protection of systems containing natural fresh waters. It is essential,

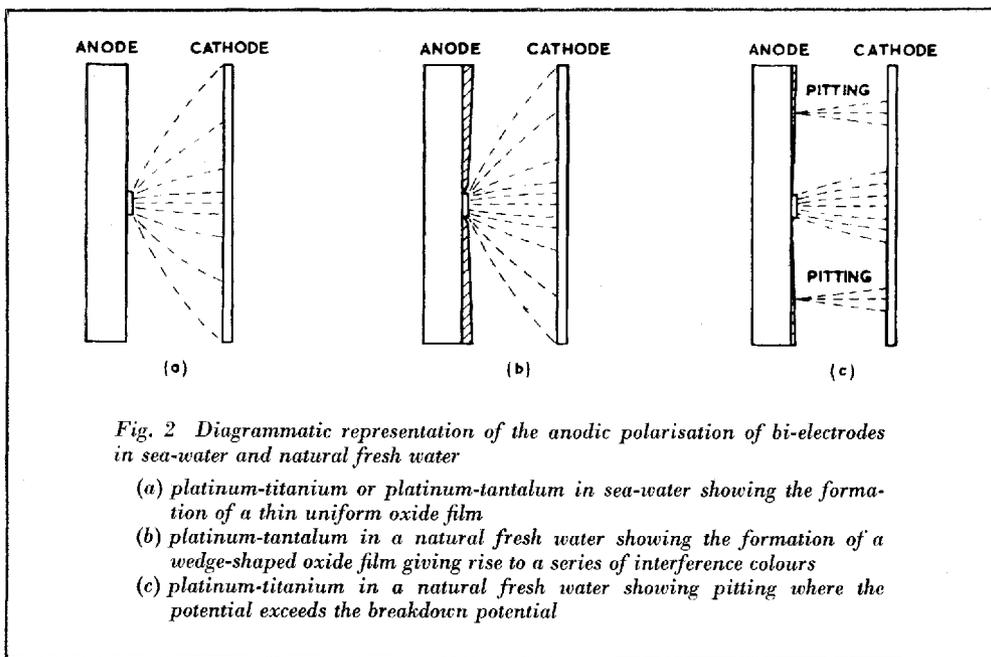


Fig. 2 Diagrammatic representation of the anodic polarisation of bi-electrodes in sea-water and natural fresh water

- (a) platinum-titanium or platinum-tantalum in sea-water showing the formation of a thin uniform oxide film
- (b) platinum-tantalum in a natural fresh water showing the formation of a wedge-shaped oxide film giving rise to a series of interference colours
- (c) platinum-titanium in a natural fresh water showing pitting where the potential exceeds the breakdown potential

however, that, if high voltages are to be used, the titanium should be completely coated with platinum.

In conclusion it should be observed that these experiments have been conducted using "commercial purity" titanium. It has recently been suggested (3) that, as a result of research

into the breakdown voltage of this purity titanium, anodes may shortly be available which will permit the use of higher voltages than 12 to 14 volts.

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Anodic Corrosion Control

A NEW METHOD OF PROTECTION BY PASSIVATION

The anodic passivation of mild and stainless steels has been applied by the Continental Oil Co., Baltimore, U.S.A., to their protection from corrosion by a wide range of acids and alkalis. The process, known as the Anotrol process, makes use of the fact that when a potential is applied to a metal immersed in an electrolyte the current passed from metal to liquid suddenly drops to a very low level when a certain critical voltage is reached. This drop results from the formation of a thin insoluble film, having a high resistivity, which confers an excellent resistance to attack by corrosive acid or alkaline media. The initial current to form the film may be large, but the period for which this is required is short—a fraction of a second. Thereafter, only a very small current is needed to maintain the passivating film.

In this process, which was described by D. A. Shock and his co-workers at a meeting of the National Association of Corrosion Engineers, the steel vessel to be protected is the anode of the electrical circuit. A specially designed platinum electrode is used as the cathode. The initial passivating current and the current required to maintain protection are supplied by a potential controller employing a calomel or silver chloride reference electrode. When in operation, the required current is automatically regulated to keep the potential difference between reference electrode and the protected vessel constant. The current requirements for initial passivation and maintenance of passivity rise with increase in temperature.

Complete success has been reported in a test conducted during the past year on a stainless steel tank used in the neutralisation of sulphonic acid by 20 per cent caustic soda solution. The severely corrosive conditions to which this tank was subjected during operation caused frequent breakdowns due to pitting before the passivation process was applied. No deterioration of the tank has been found after a year's continuous use with the Anotrol system in operation.

A further advantage of anodic passivation of chemical plant is that complex contours of vessels and pipelines may be completely protected by an electrode system situated a considerable distance from areas to be passivated. A demonstration of the "throwing power" of the system is the complete protection of a 60-foot length of $\frac{3}{4}$ -inch stainless steel tube, with fifteen bends, where both cathode and reference electrode were located in the acid container at one end.

Practical applications of this process have great potential value in the protection of steel plant employed for storing, processing or transporting a wide range of corrosive chemicals. Sulphuric and phosphoric acids, strong alkalis and aqueous solutions of oxy-acid salts have all been found to be suitable media.

Reducing systems, especially in the presence of halogens, cannot be used although some concentrations of halogens may be tolerated in oxidising conditions. Copper and copper-based alloys such as brasses and bronzes cannot be passivated.