Platinum-faced Titanium for Electrochemical Anodes

A NEW ELECTRODE MATERIAL FOR IMPRESSED CURRENT CATHODIC PROTECTION

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The good resistance of titanium to corrosion cannot be better illustrated than by its behaviour in sea-water in which it is virtually immune to attack (1), and from this it might be logical to suppose that the metal would form an excellent anode for impressed current cathodic protection of structures such as steel jetties, under-water pipelines and ships' hulls.

In point of fact, the protective surface film on titanium has peculiar properties. It is resistant to the passage of current into an electrolyte, but it has low resistivity when a second metal makes contact with it. If an attempt is made to use titanium as an anode in salt water, this resistance to the passage of current into the electrolyte immediately becomes apparent for, as shown in Fig. 1, an increasing anodic current is applied to it, the voltage required to force the current through the surface film rises until at the weakest points the film breaks down and intense local corrosion ensues. This is illustrated in Fig. 2 which records the appearance of a titanium anode after a very short operational period in sea-water at a current density of 24 amp. per square foot.

If, however, a small piece of platinum foil or wire is spot-welded to the titanium, most of the current passes out through the platinum and the titanium is uncorroded. Fig. 3 shows a composite titanium strip/platinum wire specimen which was unaffected in sea-water after carrying a current of 24 amp. per square foot for several days.

The unique property of titanium to behave

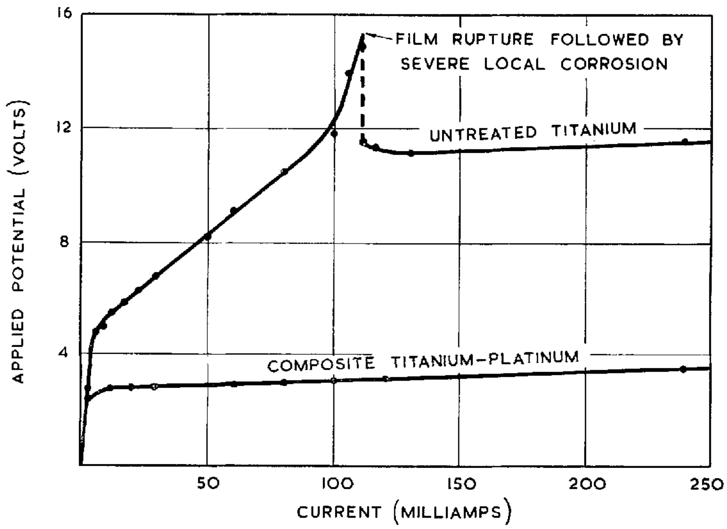


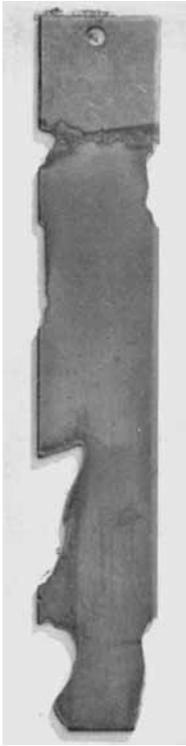
Fig. 1 Current-voltage characteristics of untreated titanium and of composite titanium-platinum in sea-water

in this manner as compared with other metals is demonstrated in Fig. 4 which illustrates the comparative behaviour of composite aluminium/platinum, titanium/platinum, stainless steel/platinum and copper/platinum, anodes after four hours' immersion in sea-water while subject to an anodic current density of 24 amp. per square foot.

Thickness of Platinum

Theoretically, the thinnest possible film of platinum should suffice to conduct current and, in fact, extremely thin films of platinum —of the order of 0.000005 inch thick—if firmly in contact with the surface of titanium, will carry high current densities without visible deterioration, even when the platinum film is porous and discontinuous. Such a film has carried anodic current densities of as high as 100 amp. per square foot in sea-water for a period of 250 hours without failure, an uncoated specimen suffering rapid corrosion in less than 30 minutes.

Evidence of the need to have noble metal actually at the anode surface and not merely to have a noble metal enriched surface is obtained if very thin films of platinum are deposited upon titanium and the composite



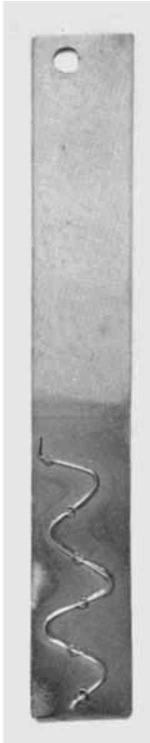
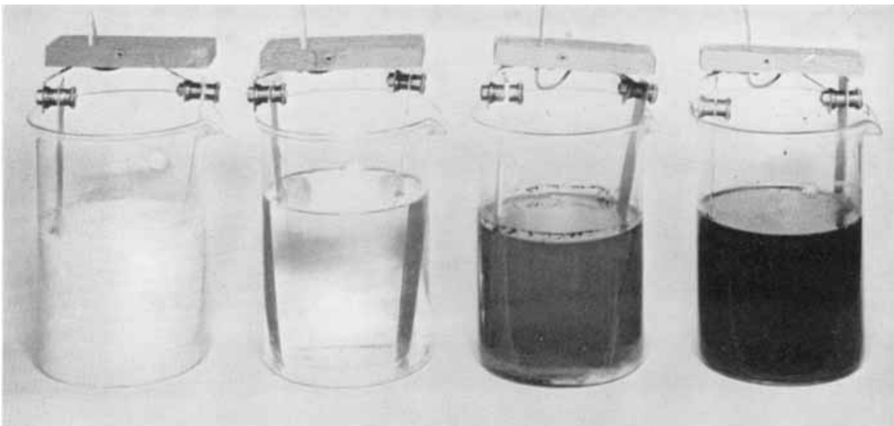


Fig. 2 (left)—Severe corrosion of titanium anode after operation for a short time in sea-water at a current density of 24 amp. per square foot

Fig. 3 (right)—Composite titanium strip/platinum wire anode after operating in sea-water for several days at a current density of 24 amp. per square foot



Composite aluminium/platinum anode | Composite titanium/platinum anode | Composite stainless steel/ platinum anode | Composite copper/platinum anode

Fig. 4 The unique property of titanium is demonstrated in this illustration, which shows beakers of sea-water containing composite anodes after four hours' service at an overall current density of 24 amp. per square foot. A titanium cathode was used in each beaker test pieces are subjected to appropriate heat treatment, such that the thin films of platinum diffuse into the titanium in varying degrees. When, after the diffusion process, these specimens are immersed in saturated brine and forced to carry an anodic current density of 100 amp. per square foot, the time to failure is entirely consistent with the extent of heat treatment; those specimens in which the platinum diffuses inwards by reason of the more rigorous heat treatment fail after a very short test period, while those having been subject to a less rigorous heat treatment and in which there is virtually no diffusion of platinum do not fail within 250 hours. Failure in this test usually takes place at the water-line and on the titanium wire connecting lead. Fig. 5 shows the condition of a series of specimens which have been subjected to the treatment just described.

For many applications it will, of course, be necessary to apply much more substantial coatings than the very thin films referred to above, but the important point is that, contrary to the situation arising when most mixed-metal systems are exposed to corrosive environments, the conjoint presence of titanium and platinum in saline solutions does not result in adverse galvanic effects upon either metal, whether D.C. current is flowing from the junction of the two or not.

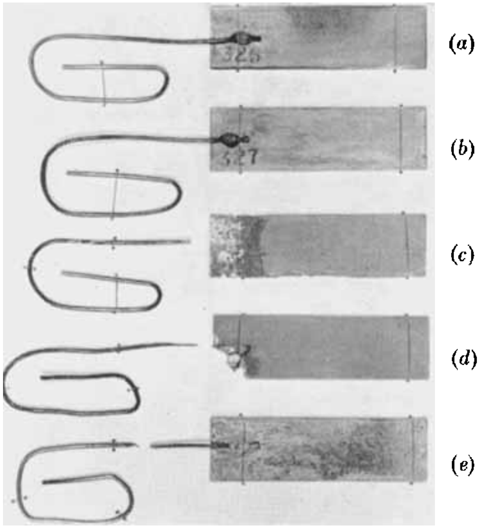


Fig. 5 Specimens of titanium coated with approximately 0.000005 inch of platinum after operation at an anodic current density of 60 amp. per square foot in sea-water at room temperature

(*a*) Not heated after coating. Greater than 250 hours without failure

(*b*) Heated in argon for 60 minutes at 500°C. Greater than 250 hours without failure

(*c*) Heated in argon for 15 minutes at 600°C. Failed after 250 hours

(*d*) Heated in argon for 60 minutes at 600°C. Failed after 70 hours

(*e*) Heated in argon for 60 minutes at 900°C. Failed after 90 minutes

Importance in Cathodic Protection

The practical consequences of these observations are likely to be of some importance. Cathodic protection is being increasingly employed as a means of preventing corrosion of chemical plant, and of structures and equipment which have to withstand marine environments. Platinum is probably the most durable anode material available, but its use is severely restricted by its high cost. The discovery that platinum can be used in conjunction with titanium considerably widens the field of use, for titanium is strong and can be formed into virtually any basic shape and size of anode, from strip, sheet, bar or wire, upon which platinum can be deposited, by a variety of methods at chosen points. The fact that the combination can withstand high anodic current densities without deterioration enhances the economic aspect, for in many circumstances it means that fewer anodes need to be used for a required area of protected metal. Titanium anodes carrying electrodeposited coatings of platinum approximately 0.0001 inch thick are on trial under actual service conditions.

Reference

1 J. B. Cotton and B. P. Downing .. Corrosion Resistance of Titanium to Sea-water, *Trans. Inst. Marine Eng.*, 1957, **69**, (8), 311-319