Cathodic Protection Applications Using Platinum Anodes

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The introduction of platinum-clad anode materials has opened up wide possibilities to the designer of cathodic protection systems. The economic advantages and excellent performance of composite anodes of platinum on tantalum or titanium are reviewed in this article.

The commercial development of cathodic protection for industrial applications has heretofore been hindered by the choice of anode materials available to the corrosion engineer. Galvanic anode materials such as zinc, magnesium and aluminium alloys have been used successfully in marine and underground cathodic protection applications but due to their relatively high cost, frequent renewal and large bulk their widespread universal use has been limited severely.

The same argument applies to the so-called impressed current or energised anode systems of cathodic protection. Although many suitable anode materials exist such as graphite, steel and high silicon-iron, and lead alloys, one deficiency or other in each of these materials has precluded their general use.

Economic Advantages of Platinum Clad Anodes

Platinum and palladium-platinum alloys, because of their unique physical and electrochemical properties, have been proposed as anode materials and have been successfully applied in several instances (1, 2). In spite of their desirable properties of electrochemical inertness, electrical conductivity and mechanical workability, the high cost generally associated with these materials has nevertheless restricted their application to specialised fields; however, in more recent years, the availability of platinum-clad materials at much reduced costs has led to increased appearance of these anodes in cathodic protection systems (3, 4, 5, 6). The cost of these platinum-clad materials was proportional to the thickness of the cladding specified and to the complexity of completely cladding difficult geometric shapes. The serious drawback to platinum-clad materials prior to relatively recent developments was that a pore-free cladding had to be applied over common basis materials such as silver or copper in order to prevent their electrochemical deterioration. Sealing the edges of clad silver or copper was also troublesome.

These objections to platinum-clad anodes were finally overcome by the commercial introduction of "rectifier" metals such as tantalum and titanium, which led to the development of platinum-coated anodes of these materials. Tantalum and titanium exhibit an interesting property when anodised in sea-water and most aqueous media. An insulating oxide is formed on the surface which gradually increases in electrical resistance until current can no longer pass into the electrolyte. These insulating oxides are stable up to certain puncture voltages, above which film rupture occurs and electrochemical deterioration of the exposed metal ensues. The oxide formed on titanium in sea-water is stable up to 12 volts applied across the film (7). Tantalum on the other hand exhibits stability up to 130 volts in certain acid media (8). However, the protective oxides on tantalum form in steps whereby a new oxide

The nuclear-powered U.S. submarine 'Seawolf', seen here with the 'Nautilus' in Long Island Sound, is fitted with an automatically controlled platinum anode cathodic protection system (Official U.S. Navy photograph)

forms at a characteristic voltage. When a rupture occurs at a particular voltage, instead of electrochemical deterioration taking place a new oxide of a different colour forms at the next corresponding voltage level and so on up to 130 volts. These protective oxides can conduct electronic current when in contact with another metal despite their non-conducting nature in an electrolyte.

The combination of platinum cladding or plating on titanium or tantalum has resulted in a low-cost anode capable of passing high current densities without deterioration of the basis metal. These platinum coatings no longer depend on continuity nor do they have to be pore-free to perform inertly. The low electrode-electrolyte interface resistance between platinum and sea-water or other conductive aqueous media permits the stable oxide layer to form on the supporting titanium or tantalum because the voltage across the oxide is kept within safe limits.

Patents relating to the use and fabrication of composite titanium and tantalum anodes have been issued during the past two decades (9, 10, 11, 12). The recent advances in inexpensive commercial production of tantalum and titanium combined with ingenious ways of applying thin layers of platinum over them has made these inert anode materials instantly available at low cost to the corrosion engineer. Platinum has been applied on these metals by rolling, plating, vapour deposition and welding.

Although tantalum and titanium anodes with 50 micro-inches thickness of vapour-deposited platinum facing have been used successfully in equipment for the electrochemical demineralisation of sea-water and brackish water, little operational evidence is available on minimum thickness of platinum required for cathodic protection purposes, for example in sea-water under velocity conditions; however, some success using 0.00025 inch of commercially available platinum rolled on tantalum has been reported (13). Research work has been proposed for examining weight loss of composite platinum-titanium or tantalum anodes under maximum current densities as a function of platinum thickness and method of coating basis materials.

Chemical Behaviour of Anode Materials

Before we get into suggested areas of application, let us compare some of the properties of platinum, tantalum and titanium as shown in the table and just mention some chemical behaviour of the materials so that the designer can be aware of some of the inherent differences between them.

From the viewpoint of cathodic protection and other allied electrochemical processes platinum is inert to electrolysis in most media, including fused salts. In fact, no single acid can attack platinum; it dissolves only in aqua regia. Platinum is extremely resistant to chlorine and oxychloride environments which make it versatile in sea-water electrolytes. It is not susceptible to hydrogen embrittlement.

Tantalum is inert to a wide variety of reagents except certain acids containing hydrofluoric acid or free sulphur trioxide. Over the temperature range commonly used in solution processes tantalum is not attacked by nitric acid, even when fuming, by hydrochloric acid, aqua regia, chlorine oxide, bromine, hypochlorous acid or hydrogen peroxide, to name a few, almost with no limitation on the concentration.

Tantalum has poor resistance to concentrated alkaline solutions and is dissolved by molten alkalis. However, dilute alkali solutions apparently have almost negligible effect. The affinity of tantalum for hydrogen makes it extremely susceptible to embrittlement. This is readily brought about when tantalum is made cathodic in a galvanic or electrolytic cell. In certain instances such as for electroanalytic copper determinations, tantalum can be used successfully as a cathode if the initial copper deposit can be made at relatively high current densities. The inert oxide film which forms on a tantalum anode is its prime characteristic in making inexpensive inert anodes for cathodic protection and chlorine production applications.

Commercially pure titanium has outstanding resistance to sea-water and marine atmospheres. It is not affected to any great extent by chlorine dioxide, sodium and calcium hypochlorite and hot metallic chloride solutions up to concentrations of 80 per cent. It is quite resistant to attack by chromic acid up to concentrations 36.5 per cent and hydrochloric acid up to 3 per cent at room temperature. The metal is rapidly attacked by hot or concentrated solutions of hydrochloric acid but is almost completely resistant in aqua regia. Titanium is attacked by all concentrations of hydrofluoric acid. Exposure to hydrogen peroxide, boiling hydroxides,

Comparative Properties of Commercially Pure Platinum, Tantalum and Titanium

	Platinum	Tantalum	Titanium
Density, gm/cc	**21.4**	**16.6**	**4.5**
Melting point, °C	**1769**	**2996**	**1660**
Thermal conductivity, C.G.S. units	**0.17**	**0.13**	**0.04**
Coefficient of expansion (0–100°C)..	**8.9×10^{-6}**	**6.5×10^{-6}**	**8.9×10^{-6}**
Specific heat, cal/gm/°C at 20°C	**0.032**	**0.036**	**0.126**
Electrochemical equivalent, mg/coulomb	**0.5058**	**0.3749**	**0.1241**
Electrical resistivity, microhm-centimetres at 20°C	**10.6**	**15.5**	**55**
Temperature coefficient of resistance, (0–100°C)	**0.0039**	**0.0038**	**0.0033**
Tensile strength—annealed, tons/in²	**10**	**22**	**35**
Young's Modulus, lb/in²	**22×10^6**	**27×10^6**	**15.5×10^6**

Potential Applications of Platinum-clad Anodes

This discussion of the general chemical resistance of platinum, tantalum and titanium serves to illustrate the potentialities of application of these materials as anodes. Cathodic protection may be usefully applied in many areas, including the following:

Marine Applications

- Ships' hulls, both active and reserve
- Hull components; propellers, rudders and fittings
- Pumping equipment and heat exchangers
- Internal and external piping
- Dock structures, piling and other submerged structures
- Cargo, ballast and bilge tanks
- Electrolytic descaling techniques

Water and Storage

- Well casings and piping
- Water storage facilities
- Deep well pumps
- Irrigation systems
- Sewage plants and piping systems

Oil Production

- Casings
- Sucker rods
- Distribution piping
- Storage facilities

Underground Soil

- Piping
- Tank bottoms
- Submerged structures
- Cable sheath

Chemical Process Industries

- Pulp and paper processing
- Production of reagents
- Breweries

nitric acid in all concentrations at elevated temperatures, or water saturated with hydrogen sulphide and sulphur dioxide, or molten sulphur has a negligible to slight effect on the metal. In fact, any oxidising substance generally does not attack titanium due to the formation of natural protective oxide film on the metallic surfaces; however, non-oxidising acids such as phosphoric acid above 30 per cent and sulphuric acid above 5 per cent, or in any concentration at elevated temperatures, attack titanium vigorously. This attack can be reduced to negligible levels by making the titanium the anode in an electrolytic cell. A potential of 1.5 volts between anode and cathode is considered a practical value (14). Titanium is not as susceptible as tantalum to hydrogen embrittlement and is readily polarised when coupled galvanically to more anodic materials.

The ingenuity of the engineer and scientist is the only limitation as to the type of anode that can be fabricated for specific application. The common forms available are plate, foil, wire, rod and tubing as well as expanded and woven mesh. Fig. 1 illustrates an expanded platinum-clad tantalum mesh anode. In addition any cross-sectional shape that is extrudable can be made for special purposes. These common forms can be fabricated as discs, rings, hemispheres and spheres, tapered wires, crimped or specially formed tubes, spirals, helices and a myriad of geometric shapes to fit compactly, neatly and efficiently into any protection scheme.

Insulating supports for these members should be a dielectric material not affected by the environment of the electrolyte in

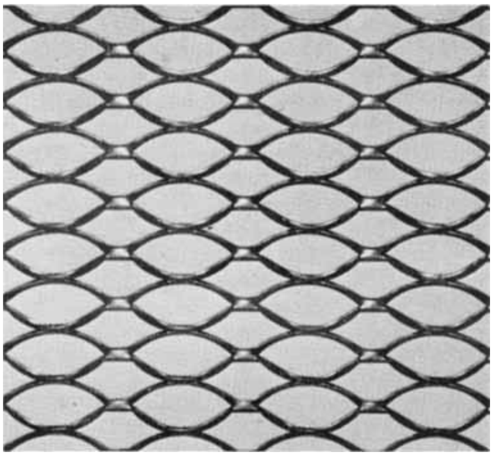

Fig. 1 Detail of expanded platinum-clad tantalum anode. Thickness of platinum is 0.00025 inch. (Metals and Controls Corporation)

which it is immersed or by the anode or cathode reaction products resulting from cathodic protection. In sea-water applications the polyester resins exhibit good chemical resistance against anode oxychloride reaction products and the epoxy resins are recommended for resistance to cathodic hydroxide reaction products (15).

Since specific designs of anodes applicable to various structures mentioned are subjects of patent disclosures, the details of construction are not available. However, two commercially produced items in the marine field are receiving widespread attention.

Protection of Active Ships

In the application of cathodic protection to active ships, a platinum-clad tantalum anode mounted in a streamlined holder has been developed. This anode holder assembly, shown in Figs. 2 and 3, consists of a seven-inch disc of 0.015 inch tantalum which has been clad with a 0.0025 inch layer of platinum. During the rolling operation the surface was embossed with a series of closely spaced squares. Embossing was used to assist easy liberation of gaseous products formed at the anode during electrolysis. The anode proper is mounted in a resistant, rigid polyvinyl chloride holder which is in the shape of a disc with an ogival cross section. A tantalum prong welded to the centre of the back of the anode disc surface protrudes from the holder. This prong mates with a connector in a specially designed waterproof stuffing

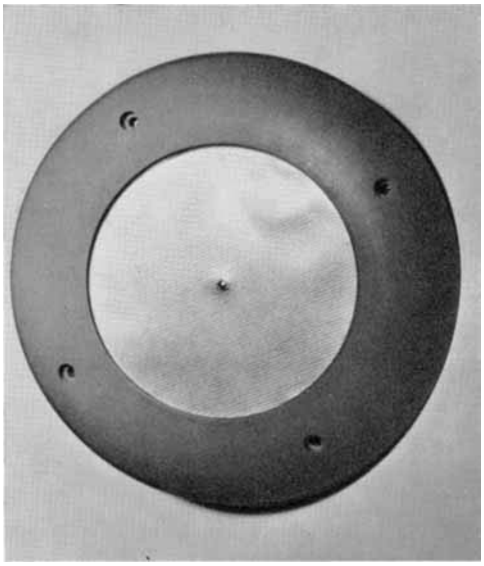

Fig. 2 A hull-mounted platinum-clad tantalum anode. The embossing of the surface assists liberation of gaseous products formed during electrolysis. (Metals and Controls Corporation)

tube which is welded into the hull. The anode is then bolted to the hull with recessed bolts which are potted over with epoxy-resin. A series of four to eight anodes are thus fitted to the hull of a ship—the number depending on the underwater area to be protected—and are connected internally to a suitable D.C. power source.

Another marketable product is the pipe plug anode used for the protection of pumps. This type of anode, shown in Fig. 4, consists of a platinum-clad disc mounted in a plastic pipe plug which terminates in a suitable con-

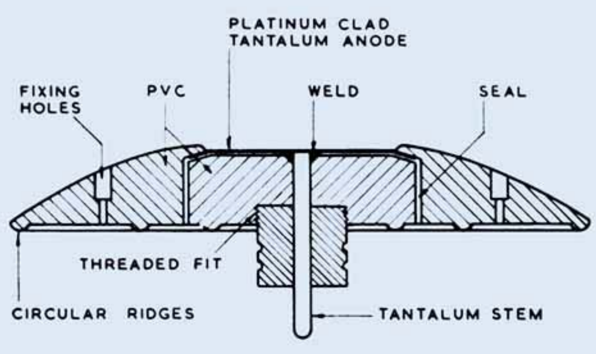

Fig. 3 Cross-section of the hull-mounted platinum-clad anode assembly shown in Fig. 2

nector. These pipe plugs are threaded into bossings fitted on a pump casing and are connected together through a harness lead to the positive side of a D.C. power supply. The negative terminal is earthed against pump casing and rotor. This arrangement will provide cathodic protection to the internals of the pump. No operational data are available, but tests on a salt water circulating pump are to be scheduled shortly.

This article is intended to focus attention on the unlimited possibilities for novel cathodic protection designs which are now open to the corrosion engineer. The economic advantages of composite anodes of platinum and tantalum or titanium, their excellent performance as inert anode materials in a large variety of electrolytes and their ease of forming into optimum geometric configurations make these truly engineering materials of a new dimension.

Fig. 4 A plug-type anode for the cathodic protection of pumps, fitted with a platinum-clad disc. (Metals and Controls Corporation)

The opinions expressed in this paper are the personal views of the author and do not necessarily reflect the official views of the United States Navy.

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