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# Tantalum Protective Thin Coating Techniques for the Chemical Process Industry: Molten Salts Electrocoating as a New Alternative

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**Abstract:** A comparison of corrosion resistance and basic properties of solid tantalum with other high-performance materials used in the Chemical Process Industry (CPI) is given. The corrosive chemicals taken into consideration are strong acidic media. Secondly, it is pointed out that tantalum, which exhibits excellent corrosion resistance, owing to a rapid build-up of passivating protective film in oxidizing conditions, also has good mechanical, thermal and electrical properties which suggest its use when little or no metallic corrosion is tolerated. Thirdly, tantalum thin-layer, coated onto a usual base metal, which offers the same protection as solid metal and avoids its expensive use, is treated. Fourthly, numerous tantalum-coating techniques for clad-vessel and CPI devices are reviewed and compared. Amongst these coating techniques, this paper focuses mainly on two techniques which give a very thin, protective coating against corrosion. Thus, Chemical Vapor Deposition (CVD) and Molten Salt Electrodeposition (MSE) are especially enhanced. Finally, MSE which is still not widely used for manufacturing clad-vessels is examined in greater detail. © 1996 Elsevier Science Limited

## 1 INTRODUCTION

In the Chemical Process Industries (CPI), engineers encounter a wide range of harsh operating conditions and corrosive chemical environments. This often makes materials specification expensive and time-consuming, requiring high-efficiency materials for the process. Actually, several CPI plants have to solve the critical problem of construction material selection. This corrosion comes from the corrosive media employed in such processes (e.g. organic and mineral acids, strong concentrated alkalies hydroxides, molten salts and liquid metals) and severe operating conditions such as high temperature and pressure.

Nevertheless, corrosion problems may exist even if process equipment does not show any visible corrosion. As a general rule, slow corrosion rates degrade the quality of fine chemicals, drugs, foodstuffs and pharmaceuticals. It can poison certain catalysts and induce catalytic reactions of certain hazardous chemicals. Finally, it can be harmful to the environment due to the toxicity of the wastes. Stainless steels, the best known corrosion resistant material, do not always guarantee immunity against corrosion.

For example, AISI 316L type stainless steel equipment with 1000 $m^2$ surface area which corrodes at a rate of 50 $\mu$m/year† (2 mpy‡), releases daily into the reactor or the environment the following amounts of metals: 712 g of iron, 186 g of chromium, 132 g of nickel, 33 g of molybdenum, and 22 g of manganese.

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†A construction material is satisfactory against corrosion in a medium when the corrosion rate is below 100 $\mu$m/year (4 mpy), which is equal for a material with a density of 8 $g.cm^{-3}$ to a weight loss of 2·2 $g.m^{-2}.day^{-1}$.

‡One mil per year (mpy) is accurately equal to 25·4 $\mu$m per year ($\mu$m/y).

Today, thee are numerous possibilities for preventing severe corrosion of CPI equipment in the area of plant design. The success of these processes depends on the selection of the construction materials that are in contact with the corrosive media.

## 2 ANTI-CORROSION MATERIALS FOR THE CPI

### 2.1 Common industrial solutions against highly corrosive media

Depending on the aggressiveness of corrosive media, there are a wide range of metallic construction materials ranging from steels to non-ferrous alloys[1] used in CPI devices. The main corrosive media usually found in chemical processes are essentially: sulphuric, nitric, hydrochloric acid and strong alkalies. So, in order to give a simplifying approach, acids (and especially sulphuric acid) are taken for example. This arbitrary choice allows one to give, for each material, an order of magnitude of corrosion rate[2] in this medium. In Table 1, several metallic construction materials are listed according to their corrosion resistance properties. The other criteria for selecting metallic construction material are mechanical, electrical and thermal properties together with cost. These criteria are therefore given in the table.

Examination of the numerous metal and alloy classes shows that only precious metals and refractory metals are suited to resist corrosion in severe operating conditions, but only the latter class is suited for a long service life under harsh conditions, with good engineering properties and moderate costs.

### 2.2 Refractory metals in the CPI

Some subgroups of inner transition metals[24] of the periodic table such as IVB (Ti, Zr, Hf), VB (V, Nb, Ta) and VIB (Cr, Mo, W) are sometimes used[25,26] as construction materials in industrial applications. These metals have the following common properties:

— they are refractory metals, where refractory means that their melting point is higher than the setting point of iron (mp 1539°C) Their melting point ranges from 1660°C for titanium to 3410°C for tungsten. Rhenium is sometimes taken into account but its use is still negligible;

— they are reactive and therefore combine strongly with oxygen, nitrogen, carbon and other meals and non-metals outside their group, and many of their properties are quite sensitive to relatively small amounts of atomic species;

— they exhibit a Valve Action (VA) property which could be defined as follows: when acting as cathodes these metals allow current to pass but when acting as anodes they prevent passage of current owing to a rapid build-up of an insulating (passivating) anodic or oxidizing protective film.

Refractory metals are used for engineering equipment and devices, in the following industrial areas:[27] the Nuclear Power Industry,[28] Pharmaceutical Industry, Chemical Process Industries,[29] Foodstuffs Industries, Marine Engineering[30] (e.g. cathodic current protection of submersed structures such as boats, harbor plants, oil-rigs) and Civil Engineering (e.g. cathodic current protection of subterranean pipelines or reinforced steel concrete). Each refractory metal is assigned to a particular application according to its chemical inertness.[31] See Table 1 for the general properties of these metals.

A general comparison of titanium, zirconium, hafnium, niobium and tantalum chemical resistance is shown in Table 2, where the corrosion rate of the five common refractory metals widely used in CPI equipment and of platinum group metals (e.g. iridium), as absolute reference, is listed for several corrosive media. This table shows that the chemical resistance of tantalum is similar to some PGM such as iridium.

The broadest range of tantalum chemical resistance is a consequence of enhancement of its Valve Action (VA) properties.[36] Actually, tantalum's protective passivating film, $Ta_2O_5$, which forms spontaneously in oxidizing conditions, exhibits more singular poperties than the other reactive metal protective oxide films (e.g. $TiO_2$, $ZrO_2$, $HfO_2$, $Nb_2O_5$). Anodic tantalum pentaoxide has an amorphous structure, is strongly adherent to metal, extremely thin (about 1–4 nm) and self-limiting of its own thickness growth. This oxide has very good dielectric properties which is the primary reason for tantalum's commercial development for highly effective electronic capacitors. Finally,

**Table 1.** Corrosion resistance classification of metallic construction materials for the CPI

| *Material class*[3,4] | *Material* | *General corrosion resistance*[5] | *Corrosion rate in $H_2SO_4$ @ RT (mass fraction)* | *Other characteristics and properties* |
|---|---|---|---|---|
| ● **Cast irons** | ● **Cast irons**<br>— Gray, white and ductile | Resistant to conc. strong acids and to caustic alkaline solutions. Rapidly corroded by dilute acid-salt solutions. | Cast irons:<br>> 1270 μm/year<br>(10% wt) | — Cheap material without any amount of strategic metal, easy to cast into complex shapes, not readily machined or welded |
| | ● **Si-cast-irons**<br>[Si(wt%) 12–18] | Si-cast irons exhibited an excellent corrosion resistance in oxidizing and strong reducing agents. | Si-cast irons:<br>130 μm/year<br>(all conc., $T <$ bp) | — very hard, brittle and thermal shock sensitive |
| | — Duriron,® Durichlor® | | | — abbrasive and wear-resistant. |
| ● **Stainless steels** | ● **Ferritic S.S.**<br>—AISI 430, 434 | Mildly corrosive dilute solutions, oxidizing acids and unchlorinated organic solvents. | 1000 μm/year<br>(1% wt) | — Easy to machine, and easy to weld. |
| | ● **Martensitic S.S.**<br>— AISI 410, 414 | Good resistance in mildly corrosive media but not in reducing acids. | 1000 μm/year | — Hardened by heat treatment. |
| | ● **Austenitic S.S.**<br>— AISI 304, 3161 | Excellent corrosion resistance in strong oxidizing chemicals especially alloys containing small amount of Mo. Poor resistance in presence of chlorides ions. | AISI 304:[6]<br>150 μm/year<br>(20% wt)<br>AISI 316L:<br>50 μm/year<br>(20% wt) | — Easy to form. |
| ● **Ni–Cr–Fe–Mo and Ni–Mo–Cr alloys**[7] | ●**Medium alloys**<br>— Carpenter® 20, Hastelloy® G3 | Better corrosion resistance than stainless steels especially in media containing chloride ions. | Hastelloy® B:<br>130 μm/year<br>(50% wt, 60°C) | — Used in plate heat-exchangers with hot concentrated sulphuric acid. |
| | ● **High alloys**<br>Hastelloy® B2, Hastelloy® C276 | Excellent resistance in alkaline solutions, brines, sea-water and HCl at all conc. and temp. without reducing agents. | Hastelloy® C276:[8]<br>380 μm/year<br>(10% wt bp) | — Resistance to mechanical and thermal shock. |
| ● **Nickel alloys** | ● **Large amounts of nickel**<br>— Inconel® 600, Incoloy® 825 | High temperature service in reducing–oxidizing environments. | 500 μm/year<br>(80% wt) | |
| | ● **Ni–Cr–Fe–Cu alloys**<br>— Illium® G, B and 98 | | > 2000 μm/year<br>(5–90% wt)<br>< 2·54 μm/year<br>(< 5% or > 90%) | |
| ● **Copper alloys** | ● **Cupro-nickel**<br>— Monel® 400, R-405 and K-500 | Highest corrosion resistance of all copper alloys. Good corrosion resistance especially in wet-fluorine and HF. | 500 μm/year<br>(50% wt) | — Good electrical and thermal conductivity<br>— ductile and cold working,<br>— difficult to machine,<br>— used in heat-exchanger tubing. |
| ● **Lead alloys**[9] | ● **Chemical lead**[10]<br>[Pb with (Sn, Bi, Sb, Te)] | Chemically inert in numerous corrosive media (e.g. chromates, sulphates, etc.) owing to rapid build-up of a passivating protective film. | 130 μm/year<br>(50% wt) | — Cheap construction material,<br>— low melting point,<br>— high thermal linear expansion coefficient,<br>— used as anode material.[11] |
| ● **Precious metals** | ● **Noble metals**<br>— Au, Ag | Excellent corrosion resistance in several corrosive media. Dissolve in aqua regia and mercury. | < 2·54 μm/year<br>(80% wt, bp) | — Very high cost. |
| | ● **Platinum group metals**<br>— Ru, Rh, Pd, Os, Ir, Pt | Exceptional corrosion resistance in all corrosive media. Ru, Rh, Ir, do not dissolve in any strong mineral acid, aqua regia and fused alkalies.<br><br>Pt, Os dissolve readily in acqua regia and mercury. Pd and Os dissolve readily in conc. $HNO_3$ | < 2·54 μm/year<br>(80% wt bp) | — Solid Pt has been used one century ago for still manufacture in the solid state[12] or as porcelain liner[13] in the lead chambers process.<br>— PGM are only used for laboratory scale device manufacture. |

**Table 1.** *contd.*

| *Material class*[3,4] | *Material* | *General corrosion resistance*[5] | *Corrosion rate in $H_2SO_4$ @ RT (mass fraction)* | *Other characteristics and properties* |
|---|---|---|---|---|
| • **Refractory metals** | • **Titanium and alloys**<br>— ASTM grades 1–4 (unalloyed)<br>— ASTM grades 5–18 (alloyed) | Excellent corrosion resistance in wet-chlorine, media containing chloride anions and in oxidizing acidic brines. But in strong mineral acids titanium exhibits a faulty corrosion resistance. | >31 750 μm/year (80% wt bp) | — Used in the chlor-alkali industry as base metal for anode materials design for chlorine evolution (e.g. DSA®),<br>— construction material in sea-water desalination plants, and in the pulp and paper bleaching plants by wet chlorine. |
| | • **Niobium and alloys**[14–16]<br>— Nb, C-103, FS-85, Nb-1Zr | Lower chemical resistance than zirconium especially in oxalic acid. | 12 700 μm/year (80% wt bp) | — Expensive and dense refractory metal,<br>— its protective oxide film has excellent dielectric properties,<br>— sometimes used as a base metal for anode material for cathodic current protection in harsh operating conditions (e.g. Protectodes®, Heraeus). |
| | • **Zirconium and alloys**[17]<br>— Zircadyne®, Zircaloy®, Zr-2·5Nb | Exhibit better chemical resistance than titanium and alloys to corrosive attack by most organic and minerals acids, strong caustics, and some molten salts. | >55 880 μm/year (80% wt bp) | — Good mechanical strength properties,<br>— Zircaloy® with extra-low Hf content are widely used in nuclear pressurized water reactors. |
| | • **Tantalum and alloys**[18–22]<br>— KBI® −6, −10, Ta-40Nb, T-111, T-222 | Chemical resistance of tantalum[23] has broadest range of inertness with respect to chemical and thermal breakdown susceptibility | <2·54 μm/year (80% wt bp) | — High density and high cost. |

**Table 2.** Corrosion resistance of Ti, Zr, Hf, Nb, Ta and Ir in some corrosive media[32] expressed in μm/year (to convert μm/year to mpy divide by 25·4)

| | *Metal* | | | | | |
|---|---|---|---|---|---|---|
| *Corrosive chemical* | *Titanium* | *Zirconium*[33] | *Hafnium* | *Niobium*[34] | *Tantalum*[35] | *Iridium* |
| • HCl 37% (fuming) @ 60°C | Poor (>1250) | Excellent (<25) | Excellent (<25) | Poor (250) | Excellent (<2·54) | Excellent (<2·54) |
| • $H_2SO_4$ 80% (boiling) | Poor (>1250) | Poor (>500) | Poor (>500) | Poor (5000) | Excellent (<2·54) | Excellent (<2·54) |
| • $HNO_3$ 70% (boiling) | Good (<125) | Excellent (<25) | Excellent (<25) | Excellent (<25) | Excellent (<2·54) | Excellent (<2·54) |
| • KOH 50% (boiling) | Poor (2700) | Excellent (<25) | Excellent (<25) | Poor (>300) | Poor (>300) | Excellent (<25·4) |
| • $H_2O_2$ 30% (boiling) | Poor | Excellent (≈0) | Excellent (≈0) | Poor (500) | Excellent (<2·54) | Excellent (<2·54) |
| • $H_2C_2O_4$ 10% (boiling) | Poor (>1250) | Excellent (<25) | Excellent (<25) | Poor (1250) | Excellent (<2·54) | Excellent (<2·54) |
| • Aqua regia (3 HCl: 1 $HNO_3$) | Excellent (0) | Poor (>1250) | Poor (>1250) | Excellent (<25) | Excellent (<25·4) | Excellent (<25·4) |
| • HF 10% @ RT | Poor (>1250) | Poor (>1250) | Poor (>1250) | Poor (>1250) | Poor (>1250) | Excellent (<2·54) |
| • Mineral acids (with 200 ppm $F^-$) | Poor (>1250) | Poor (>1250) | Poor (>1250) | Poor (>500) | Poor (>500) | Excellent (<2·54) |

$Ta_2O_5$ is formed and persists even in extremely oxygen deficient environments. Nevertheless, tantalum immunity is lost when the metal is in contact with reagents which prevent or slow down oxide layer formation or damage this natural barrier. For example, hydrofluoric acid and fluoride ions, sulphur trioxide and *a fortiori* fuming sulphuric acid, concentrated strong alkali hydroxides and fused carbonates rapidly attack tantalum metal.

According to this overview of its chemical resistance, tantalum is an inescapable construction material for chemical equipment submitted to hot and concentrated strong acis (e.g. sulphuric, nitric, hydrochloric, hydrobromic) and when no corrosion products are tolerated.

## 2.3 Tantalum selection

Some important physico-chemical properties of the pure chemical element are presented in Table 3. For more detailed properties, it is possible to refer to specialized textbooks.[38,39]

Close examination of Table 3 shows that besides its excellent corrosion resistance, tantalum metal exhibits numerous physical properties of interest to chemical engineers. These properties are suited for industrial use in CPI equipment. These additional assets bring tantalum closer to other high-performance metals and alloys used in industrial applications. A better electrical conductivity compared to other common refractory metals (e.g. Ti, Zr) is responsible for its use in association with niobium as base metal for platinized-anodes[40] as a replacement for titanium[41] (e.g. Protectodes,® Heraeus). These anodes are widely used for cathodic current protection in sea-water and are suited to large surface area plants and vessels (e.g. tankers, oil-rigs) when localized anodic current densities reach several $kA.m^{-2}$. Tantalum is also employed as a base metal in DSA® type electrodes[42,43] In some electrochemical processes working in harsh conditions.[44] Its good thermal conductivity gives a suitable construction material when corrosion resistance has to be combined with good heat transfer conduction. Thus, tantalum is widely used for heat transfer devices working in concentrated acidic media (e.g. plate and tube heat exchangers, bayonet heaters and thermowells, etc.). Its good tensile strength is required for the manufacture of some devices (e.g. rupture disks, impellers). For example, some distillation columns of concentrated strong mineral acids have tower internals in solid tantalum (e.g. Ta-Intalox®).

In conclusion, tantalum exhibits exceptional properties[45] and for these reasons it is used in harsh operating conditions and when no corrosion products are tolerated. It is therefore often used in pharmaceutical, biotechnological and foodstuff processes.[46] In particular conditions, some tantalum alloys like KBI® −6, −10,[47] −40 supplied by Cabot Performance Materials Inc. are chosen. These alloys, containing especially 2% W, 10% W and 40% Nb by weight, are sometimes used for their better mechanical properties than solid tantalum but they have a higher cost. They serve for fittings and valve internal fabrication. Finally, by analogy with glass chemical resistance, they are sometimes used for assembling pipes in glass-lined technology.

**Table 3.** Tantalum chemical element miscellaneous properties[37]

| *Physical properties of the metal* | | |
|---|---|---|
| Chemical abstract registry number | [7440-25-7] | |
| Electronic structure | $[Xe]4f^{14}\ 5d^3\ 6s^2$ | |
| Atomic number | 73 | |
| Relative atomic mass ($^{12}C=12$) | 180·948 | |
| Density ($\rho$/kg.m$^{-3}$) | 16654 | (293 K) |
| Spatial group (lattice) | Im3m | (body centred cubic |
| Lattice parameters ($a$/pm) | 330·29 | |
| Melting point ($T$/K) | 3269 | |
| Electrical resistivity ($\rho/10^{-8}\Omega$.m) | 13·5 | (293 K) |
| Thermal conductivity (k/W.m$^{-1}$.K$^{-1}$) | 54·4 | (293 K) |
| Thermal expansion coefficient ($\alpha/10^{-6}$ K$^{-1}$) | 6·6 | |
| Young's modulus ($E$/GPa) | 185·7 | (polycrystalline) |
| Bulk modulus ($K$/GPa) | 196·3 | (polycrystalline) |
| Poisson ratio | 0·342 | (polycrystalline) |
| Tensile strength ($R_m$/MPa) | 345 | (polycrystalline) |
| Thermal neutron cross-section ($\sigma$/barn) | 20·5 | |

## 2.4 Tantalum thin-coating

Today, most industrial tantalum equipment proposed by specialized suppliers (e.g. Cabot,

NRC, Degussa, Danfoss) is made from 0·75 mm thick solid tantalum plates. In the previous paragraph, it was shown that solid tantalum exhibits singular properties but it also has two great drawbacks: high density and high cost.

According to corrosion studies performed by Danzig *et al.*,[48] a thin tantalum coating (100 $\mu$m) provides excellent corrosion resistance for the base metal. So, it is economically advantageous to use a thin layer of tantalum clad onto a common base metal. Today, some clad vessels for CPI are made with an ordinary base metal (e.g. steel, copper) coated with tantalum.[49,50] A price comparison of several protective solid metals contained in a thin metallic layer of 100 $\mu$m thickness on a unit surface area of one square meter is given in Table 4.

Examination of Table 4 shows firstly that more economical coatings (e.g. Ti, Zr, Nb) than those made with tantalum are unsatisfactory in harsh corrosive media such as boiling and concentrated sulphuric acid. Secondly, amongst the excellent metallic protective coatings against corrosion, tantalum coating is the least expensive.

Today, there are numerous coating or cladding techniques available for tantalum thin layer deposits.[54] The following section gives a rapid and concise overview of all these techniques.

## 3 TANTALUM THIN-COATING TECHNIQUES

### 3.1 General properties of thin-coating

A metallic thin-layer coated onto an ordinary base metal, offers all the advantages of solid metal such as surface properties[55] (e.g. corrosion resistance, hardness), and avoids the expensive use of solid metal. This allows for a wide diversity of base metals and therefore for the employment of a common and cheap metal (low cost, low density, easy machining, etc.). For example, common metals suitable as the base metal are: carbon steel, cast-iron, mild steel, stainless steels, aluminum, copper, nickel and titanium.

Metallic coatings have a broad range of applications besides corrosion protection, moreover the main principle is always the same:[56] fabricate a composite material with sandwich type structure which exhibits surface properties different than the overall solid material.[57]

Amongst the several classifications of metallic coating techniques, a description of coating techniques by physicochemical principles has been adopted. Today, the following techniques[58] for metallic coatings are available: mechanical, physical, chemical and electrochemical.

Some criteria requirements in thin deposit techniques are: preparation of base metal, deposition rate, base metal limitations (e.g. geometry, size, temperature, compatibility, etc.), structure and coating-adherence to base metal and throwing power. Economical criteria are: simple plant design, low maintenance costs and minimal capital cost.

As a general rule, metallic coating formation decomposes into three successive or simultaneous steps as follows: (i) production of specie(s); (ii) mass transfer of the specie(s) from source to base metal surface; and (iii) deposition on the base metal and crystalline-growth of the coating.

**Table 4.** Cost comparison of thin coatings protection against corrosion in harsh media

| *Metal* | *Cost* $(C/\$.kg^{-1})$[51,52] | *Density* [293 K][53] $(\rho/kg.m^{-3})$ | *Cost of 100 μm thin coating* $(c/\$.m^{-2})$ |
|---|---|---|---|
| Titanium | 250 | 4540 | 113 |
| Zirconium | 360 | 6506 | 234 |
| Niobium | 540 | 8570 | 463 |
| Tantalum | **740** | **16654** | **1232** |
| Hafnium | 1630 | 13310 | 2170 |
| Iridium | 4900 | 22560 | 11054 |
| Platinum | 17400 | 21450 | 37752 |

### 3.2 Mechanical cladding processes

The mechanical cladding techniques described here are based on simple physical principles. Their straightforwardness explains their widespread use in the industrial forming of clad-vessels for CPI.

*3.2.1 Loose-lined construction*

Tantalum liners may be manufactured separately and inserted into vessels without bonding with the base metal. This loose-lined construction is the most economical and widely used fabrication method. Liner thicknesses of

0·4–0·8 mm are satisfactory against corrosion. It is also possible to improve this technique by welding the liners to the base metal (so-called weld overlay).

Although economical, loose-lined construction has some intrinsic drawbacks: (i) unsuitability for vacuum use; (ii) limitation with regard to temperature and pressure; (iii) poor heat transfer coefficient due to the air space between liner and base metal; (iv) difficulty in failure inspection and control and (v) larger thickness of the liner than the 100 $\mu$m is required. This technique therefore needs large amounts of expensive solid tantalum plates.

*3.2.2 Roll bonding and hot rolling*

Roll-bonding is a mechanical method of joining metals by applying pressure sometimes combined with heat, with or without the use of a filler metal. The clad metal plate and backer, sometimes with intermediate material in order to ensure good bonding, pass through two heavy rollers. When rolling is complete, the sandwich cladding plates are obtained. In this technique, good ductility of the coating metal is the main property required for good bonding. Thus, tantalum must be very pure [Ta(%wt) > 99·9], because small amounts of interstitial elements (e.g. C, N, O) would have catastrophic effects on ductility. It is possible to work at high temperature in order to increase the plastic deformation process, but the high temperature requirements (1000°C) lead to work in an inert atmosphere in order to prevent oxidation of reactive metals like tantalum which form tenacious oxide surface films. This means that tantalum roll-bonding is not possible in air.[59] In order to avoid thermal oxidation film formation during heating, the tantalum roll-bonding process can also be performed in vacuum.[60] With this technique, the minimum cladding thickness is about 1·5 mm. For certain special procedures, tantalum-lined vessels are being produced with 0·25–0·38 mm thick elastomer bonded tantalum sheet on steel plate.

*3.2.3 Explosive bonding and cladding*

Explosive cladding,[61] or explosion bonding and explosion welding, is a method wherein the controlled energy of a detonating explosive[62] is used to create a metallurgical bond between two or more similar or dissimilar metals.[63] No intermediate filler metal is needed to promote bonding and no external heat is applied. Explosive bonding is a cold pressure-welding unlike fusion welding. During the process, the bonding is performed by high pressure collision of two metallic plates jetted together. Areas as small as a few square centimeters to several square meters have been bonded. Limitations of the explosive bonding are listed below: (i) storage and handling of explosives can be hazardous; (ii) when there is a large difference of density between metals a high quality bonded interface is difficult to achieve and so a filler material is needed; (iii) complex geometries are not suited to explosive bonding because of the high velocity jet expelled; (iv) the preparation and assembly of clads is not amenable to automated production techniques, and each assembly requires considerable manual labor; and finally (v) coating thickness is equal to millimeters as an order of magnitude which requires large amounts of solid tantalum.[64]

*3.2.4 Thermal spraying techniques*

Thermal spraying methods are used in a wide range of industrial applications.[65] The coating is obtained by projection of molten metal droplets which are carried by compressed gas toward the workpiece. Droplets of liquid metal are obtained by melting metal powder. The size of the powder particles ranges from 10 to 125 $\mu$m. Particles are carried by an inert gas (e.g. argon) to a heating source. The heat of the source melts the metal and accelerates it toward the workpiece where particles fuse as interlocking laminates, each layer being fused to the previous one.

The following heating techniques can be used: oxyacetylene-flame (2800°C), detonation (3000°C) or electric arc (4000°C), and sometimes a high frequency plasma or laser. In the particular case of tantalum only a high temperature source and inert atmosphere are suitable owing to its high melting point and high chemical reactivity with oxygen and nitrogen. Thus arc-spraying, plasma-spraying and detonation gun in a protective gas overcome the limitations of the flame spraying process.

Detonation gun, plasma- and arc-spraying give adherent coatings. Nevertheless, due to its mosaic structure with some defects (e.g. amounts of oxide, vacancies), a sizeable deposit thickness (about 1 mm) is required to protect the base metal against corrosion attack. This

great thickness of the coating leads to large amounts of expensive solid tantalum being required. The high costs of the detonation gun process associated with the expensive amount of tantalum come close to the costs of solid metal manufacture.

Therefore, the mechanical techniques described, in spite of their straightforwardness, have great drawbacks. They need large amounts of solid tantalum, are unsuitable for complex workpiece cladding and need heavy equipment. Furthermore, the preparation of clad-assemblies is not amenable to automated production techniques and each assembly requires considerable preparation.

### 3.3 Physical coating processes

Physical Vapor Deposition (PVD) allows a thin coating to be obtained under diminished pressure and low temperature (typically ranging from 50 to 500°C). This characteristic makes it possible to apply extremely thin metallic coatings onto workpieces ready to use (e.g. tempered, machined).[66] Dimension variations are therefore low after treatment and quite restricted to the thickness of the deposit. Only two PVD methods are suitable for thin tantalum-coatings, as mentioned below.

#### *3.3.1 Vacuum deposition*

The principle of vacuum deposition or evaporation is as follows: in a chamber under high vacuum ($10^{-2}$–$10^{-1}$ Pa), vapors of coating metal are produced by heating a metal sample. The vapor is expanded into the vacuum toward the surface of a precleaned base metal. Metallic atoms reach the workpiece by mass diffusion transfer and are condensed in a solid phase onto the cold base metal. Two kinds of heating source are available: (i) *direct* by resistance heating known as the Joule effect. The metal is contained in a crucible heated by a spiral coil or is deposited onto a refractory filament (e.g. Mo, W) submitted to high electric current flow; (ii) *indirect heating*, where the temperature is raised in order to produce atomic vaporization of the metal using the following techniques: electron beam heating, laser beam irradiation, electric arc heating and induction heating.

The deposition process is achieved under high molecular vacuum to avoid atomic collisions with the background gas. So, free atoms have a quasi straight-line trajectory from source to workpiece.

Tantalum vacuum coating requires harsh experimental conditions owing to the refractory properties of tantalum (mp 2996°C). Thus, tantalum should be heated above 3350°C in order to get a vapor pressure above 13·33 Pa (0·1 mm Hg).[67] Only electron beam heating usually allows this high operating temperature to be reached.

The advantage of this technique, which gives coherent tantalum deposits, is the high deposition rate (75 $\mu$m/h) combined with simple pilot design (high-vacuum chamber, vacuum pumps, heating device). These characteristics are only attractive for producing tantalum coating on the laboratory scale.

Nevertheless, deposits are often poorly adherent and extremely thin (5 $\mu$m). These drawbacks mean that the protection of the base metal against corrosion cannot be guaranteed. Moreover, vacuum deposition is directional; so only the front side of the workpiece is coated which leads to poor throwing power. Finally, high vacuum operating conditions are very difficult to achieve on an industrial scale for large coating equipment.

#### *3.3.2 Cathodic sputtering deposition*

The cathodic sputtering deposition[68] principle is the following: in an inert gas (e.g. argon) chamber, under reduced pressure ($1 \times 10^{-2}$ Pa), a sparkly discharge is produced by a high-voltage application of several kilovolts between the cathode (target) and the anode (base metal); in these conditions, argon atoms are ionized and give a luminescent discharge. A beam which is produced by argon ions accelerated by the high field strength arrives at the cathode. The kinetic energy ranges from 0·1 to 10 keV. Under incident ion impacts, the target atoms are ejected by linear momentum transfer and deposited on the anode. The kinetic energy of the ejected atom is several eV which is 10 times the kinetic energy of a vaporized atom at 1000°C. Thus, this higher energy than vacuum evaporation allows metallic bonding to increase between the coating and the base metal.

Cathodic sputtering has a low throwing power which prohibits its use for complex geometry workpieces. Nevertheless, it is suitable for tantalum deposition but the deposition rate is low (2 $\mu$m/h)[69] combined with a maximum thickness

of some micrometers. So, it is not suitable for industrial uses.

To conclude, PVD techniques have great advantages with respect to mechanical methods. They allow a thinner coating than previous techniques which causes less metal consumption and they therefore give cheap composite materials. Nevertheless, a thinner coating does not guarantee corrosion immunity to the base metal even if the coating is adherent. Moreover, experimental operating conditions are unsuitable for producing large scale coated equipment which excludes them from competitive techniques for manufacturing clad-vessels.

### 3.4 Chemical coating processes

*3.4.1 Chemical Vapor Deposition (CVD)*

The deposit is obtained by chemical reaction between a gaseous reactant at the base metal surface. The decomposition temperature ranges from 600 to 1200°C.

For example, tantalum coating with the CVD process is obtained by reduction of tantalum pentafluoride by hydrogen according to the following chemical reaction:[70]

$$2TaCl_5 + 5H_2 \xrightarrow{1000°C} 2Ta + 10HCl$$

The experimental conditions, which are given with greatest detail by Spitz & Chevallier[71] are the following: base metal surface temperature ranging from 1000 to 1100°C, reactive atmosphere made up of a mixture of gaseous $TaCl_5$ and an excess of hydrogen, tantalum pentachloride is obtained by *in situ* direct chloration before introduction into the reactor. Chlorine gas flows over heated tantalum flakes in a small auxiliary reactor.

The deposition rate ranges from 1 to 10 $\mu$m/min.[72] Thin tantalum coatings obtained by CVD are coherent, adherent and have good corrosion resistance properties. This technique has allowed for the production of coherent tantalum coatings 20–30 $\mu$m thick which provide adequate acid corrosion resistance. This has been deposited on the inner surface of long carbon steel pipes.[73]

Nevertheless, CVD has some drawbacks: the crystalline structure, thickness and adherence of the deposit are very sensitive to the base metal temperature and gaseous stream. A deposition temperature of 1000–1100°C results in a loss of the mechanical strength of Fe- and Ni-based alloys. For complex geometry workpieces, good temperature and gaseous stream rate control are difficult to obtain, the reactor vessel size has to be adapted for large workpieces, the reactant gases are synthesized *in situ*, it is a high-cost plant, there is a loss of large amounts of tantalum which deposit on the reactor walls, and unreacted and waste products have to be recovered on exit (e.g. HCl).

Tantalum-coated vessels have been performed by CVD process on an industrial scale by US companies such as General Technology, Ultramet, Allbright & Wilson[74] and Fansteel. For example, there are US patents covering thermowell and bayonet heater manufacture.[75–77] Sometimes a filler metal like titanium or copper is inserted between the base metal and the coating to ensure good adhesion or to prevent formation of tantalum carbide in the boundary region with a carbon steel base metal.

### 3.5 Electrodeposition process

This process for metallic deposit by electrolysis, known as Electroplating,[78] uses electrochemical reduction of metal ions present in the electrolyte. This technique allows thin coatings to be prepared with a closed controlled thickness according to Faraday's law.

Industrial Electroplating Processes (so-called Galvanizing) commonly use aqueous media for common metal electrodeposition (e.g.: Zn, Cu, Ni, Pb).[79] Aqueous electrolytes have a narrow potential span which make them unsuitable as an electrodeposit on highly electropositive metals. Actually, when cathodic potentials are applied to the electrode, the electrochemical reduction of protons occurs with hydrogen evolution. This main reaction uses the major part of the reduction current. In spite of certain cathodic materials which exhibit large hydrogen evolution overpotentials (e.g. Zn, Cd, Hg, Pb), it is quite impossible to electrodeposit such metals except certain cases concerning tantalum. Actually, tantalum deposits have been obtained in aqueous alkaline media but these deposits were only 2 $\mu$m thick and had poor coherence.[80]

Despite their wide potential span, organic media with an appropriate supporting electro-

lyte have not been studied and are not used for electroplating owing to their low electrical conductivity which increases the Ohmic drop between electrode gap.

By contrast, molten salt based electrolytes are suitable for the electrodeposition of refractory metals.[81] The wide potential span of ionic liquids between decomposition limits[82] allows the deposition of these highly reactive metals. The various reasons for these results are listed below:[83] a wide potential span of fused salt metal. The high temperature leads to fast electrochemical reaction kinetics. The Faradaic efficiencies are close to 100%. The melts have high electrical conductivity which minimizes the Ohmic-drop. Coating adherence is enhanced by etching the base metal with molten salt and/or interdiffusion phenomena. The high solubility of electroactive species allows one to work with a high solute content. Good wetting of the cathode by molten electrolyte gives good throwing power.

As a general rule, two methods are available to perform molten salt electrodeposition: (i) coherent deposit and (ii) alloyed deposit with base metal.

The *Coherent Deposit Process* (electroplating process) gives a dense, smooth and adherent coating. It is performed by classic electrolysis. Operating conditions are under galvanostatic control with two electrodes: a soluble metal anode and a cathode as the base metal (cf. Fig. 1).

The main characteristics of the coherent deposition process are: (i) the concentration of electroactive species is maintained as a constant by an anodic metal dissolution process; (ii) the rate of electrochemical reduction is given by the cathodic current density; and (iii) as a general rule, there is no limitation on the deposit thickness, nevertheless the formation of dendrites, which increase roughness and could lead to short circuits in the case of a narrow gap between electrodes, should be avoided.

Alloyed deposits with base metal by *Metalliding Process* (also known as *Electrolyte Cementation, Surface Alloying* or *Diffusion coating*) in molten salt is a process in which metallic ions are transferred to the cathode surface where they are reduced in the alloying state with base metal.[84–86] There are two methods for obtaining a surface alloy using metalliding processes.

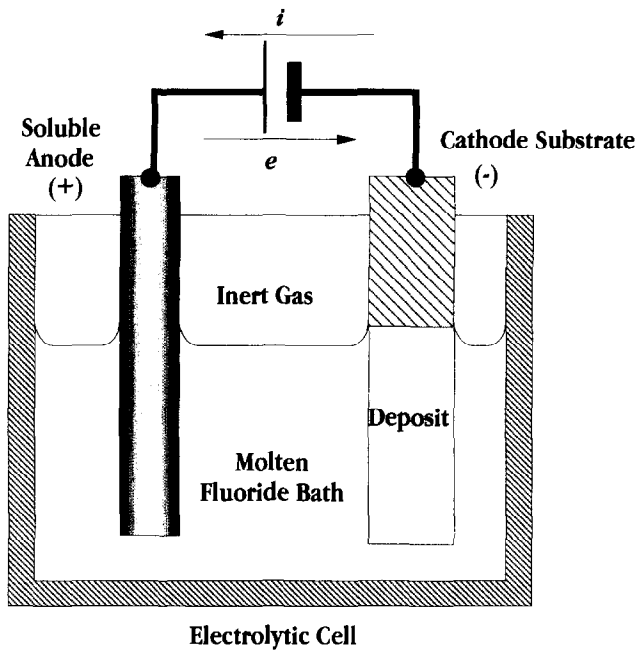



**Fig. 1.** Tantalum electroplating process.

(i) Firstly, a simpler method consists of connecting electrically the electrode which is made of the metal to be deposited (anode) with the base metal electrode (cathode) to give a galvanic cell (cf. Fig. 2). When the short-circuit is well established, the redox reaction occurs in which more electropositive metal is oxidized at the anode and gives metal ions which are reduced at the cathode by outer circuit elec-

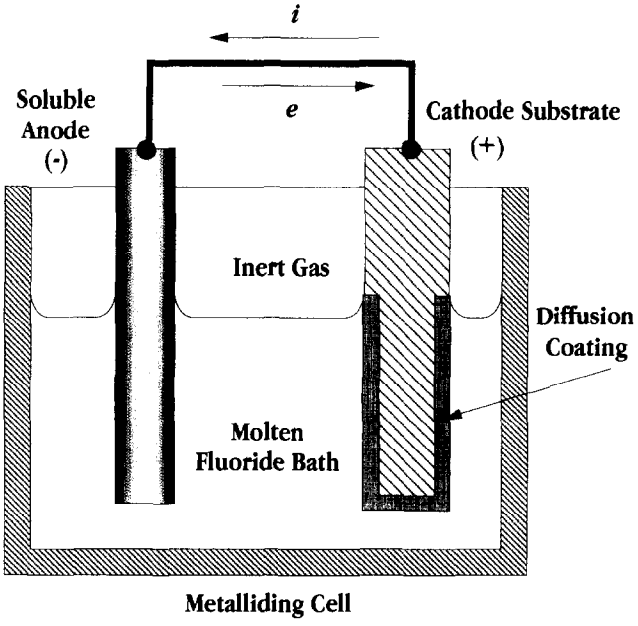



**Fig. 2.** Tantalum metalliding process.

trons and give metal alloying. The sufficient condition for ensuring good metalliding reaction is that the deposited metal must be more electropositive (resp. less noble) than the base metal. Thus, the metalliding process is self-supporting by galvanic cell electromotive force and no external electrical potential is needed. Cathodic current densities which depend on the species' diffusion coefficients range from 1 to 20 $mA.cm^{-2}$.

(ii) In the second method the alloying could also be obtained in the following two steps: (1) firstly, short-time electrolysis gives a thin metal coating on the base metal; (2) electrolysis is stopped and the cathode is maintained immersed in the melt for several hours to allow deposit of metal–base metal interdiffusion. Process validity is close linked to the two metals' interdiffusion facilities at the operating temperature (800–1100°C). For these reasons metalliding is limited to certain metals. Alloyed deposits are uniform, dense, non-porous and smooth. Stabilized alloyed deposits could be solid-solutions or intermetallic-compounds. The precursors for metalliding in molten salts are from Cook of General Electric[87–90] and Ilyushchenko *et al.*[91] The deposition mechanism in the particular case of tantalum and niobium onto nickel base metal has been explained by Taxil *et al.*[92–94]

In conclusion, refractory metals could be deposited onto a base metal by electrochemistry in molten salts. Electrodeposits are uniform, dense and adherent, however, in some particular cases they could form inter-diffusion alloys. Like CVD, MSE is a suitable technique for obtaining thin protective deposits. In the following paragraph, tantalum electrodeposition by molten salt is described.

## 4 MOLTEN SALTS ELECTRODEPOSITION OF TANTALUM

### 4.1 State of the art

Development of tantalum electrochemistry in molten salts is closely linked with refractory metals electrochemistry. The first studies on tantalum recovery in fused salt by electrolysis appeared in 1931[95] and concerned metal electrowinning. During this period 1930s–1940s, electrowinning was the only way of recovering tantalum metal from ores. Tantalum electrochemistry in molten salt underwent rapid expansion in the period 1950–1965. The great number of references on the subject concern academic studies on fundamental aspects (e.g. mechanisms, kinetic parameters), and numerous industrial patents (e.g. Norton Co.,[96–101] Union Carbide Corp.,[102,103] Horizon Titanium Corp.,[104–109] Timax Corp.,[110] Ciba Ltd,[111–114] Péchiney,[115] SOGEV,[116] Mitsubishi Heavy Industries[117]). This large development of tantalum metallurgy is the result of major military, nuclear, spatial and aeronautical programs which have involved high refractory material studies for balistics, equipment used to handle liquid metals or molten salts in nuclear power reactor systems, thermal shields for aerospace engines and a selection of high efficiency electronic devices. A wide range of melts and mixtures has been explored for tantalum electrorecovery ranging from tantalum pentaoxide diluted in cryolithe melt[118] to tantalum fluoride dissolved in chloride or fluoride melts. However, for electroplating applications, the selection of molten alkaline fluorides was highlighted by industrial studies especially those performed by the two precursors Senderoff and Mellors[119] from Union Carbide Corp. Actually, they showed that in molten alkaline fluorides, refractory metal electrodeposits were dense, coherent and adherent. Since the 1960s, these engineers have carried out a complete review of most of the reactive metals (e.g. Zr,[120] $ZrB_2$,[121] Nb,[122,123] Ta,[124] Mo and W[125,126]). The tailored operating conditions are protected by patents.[127,128] According to their patents the optimum operating conditions were the following: a bath obtained from melting the ternary eutectic mixture LiF–NaF–KF (so-called Fli-NaK) with a solute content of $K_2TaF_7$ ranging from 15 to 40% wt under inert atmosphere, at 800°C, cathodic current density of 40 $mA.cm^{-2}$. Another optimum condition for tantalum electroplating was given later by Balikhin[129] and Balikhin & Sukhoverkov[130] which use LiF–NaF–30% $K_2TaF_7$ at 800°C, cathodic current 60 $mA.cm^{-2}$ give 150 $\mu$m tantalum onto copper and steel. These coatings are coherent and non-porous with a Vickers hardness Number of 110–120.

The mechanism of electrochemical reduction of Ta(V) in these melts has been discussed; a detailed discussion about tantalum reduction in

fluoride melts has been reviewed by Polyakova *et al.*[131]

Taxil & Mahenc[132] have shown that in a fluoride melt at 800°C the reduction mechanism only occurs in one step as follows:

$$TaF_7^{2-} + 5e^- \rightarrow Ta^0 + 7F^-$$

As a general rule, the advantages of tantalum electroplating in molten salts are: high purity tantalum, which is obtained by electrorefining using a soluble anode, and a high current efficiency equal to 100%.

MSE allows one to coat several base metals such as steels, and other common construction materials.[133,134] The production of tantalum coatings 1 cm thick has also been described in the literature.[135]

### 4.2 Choice of the melt

The basic criteria required for selecting an electrolytic melt are as follows: low vapor pressure, low melting point, high electrical conductivity, low absolute viscosity, wide range of electric potentials, low corrosiveness for cell construction materials, easy to purify and low cost.

As a general rule, inorganic halogenide salts satisfy all these criteria.[136] Amongst the several compounds tested[137] rare earth (e.g. La, Ce), alkaline (e.g. Li, Na, K, Cs) and alkaline–earth (e.g. Be, Mg, Ca, Sr, Ba)[138] metal chlorides and fluorides, above all, are the most suitable compounds. Therefore, without moisture and oxygen these inorganic salts give high stability melts. Actually, molten fluorides (resp. chlorides) are very sensitive to moisture and oxygen contaminants. With water, the reaction gives highly corrosive hydrogen fluoride (resp. hydrogen chloride) which readily corrodes cell material.[139] With traces of oxygen, fluoride anions give oxifluoride complex anions which react with low-valency cations of the metal and give a protective polymeric film onto the cathode which inhibits good deposition.[140] Molten alkaline fluoride baths are now preferred for electroplating of refractory metals. Actually, fluoride melts exhibit good physicochemical properties suited to molten salt electrodeposition of these metals.[141,142] They have a low melting point especially if they are used in eutectic mixtures and with a low vapor pressure. On the other hand, fluoride ions exhibit excellent complexation properties, especially with refractory metal cations. This strong field complexation increases the high valency cation stability in the melt and avoids disproportionation reactions which could occur during the reduction process. Finally, fluoride melts have strong etching properties on removal of metallic oxide films and so avoid the formation of oxide layer onto the cathode surface. These two characteristics are very favorable for achieving coherent, dense and adherent tantalum deposits onto the base metal. By contrast, the ability of molten fluorides to remove protective oxide from most metallic surfaces is a strong drawback for the selection of good containers for these baths (it will be discussed in the following paragraph).

In practice, only alkaline fluoride melts such as lithium, sodium, potassium are widely used, in eutectic mixtures, with a ternary (LiF–NaF–KF so-called FliNaK), or binary (e.g. LiF–NaF, LiF–KF, NaF–KF) composition. The high hygroscopicity of KF, prohibits its use and in practice the binary eutectic LiF–NaF is selected for industrial uses.

In the melt, tantalum appeared as the complex[143] species $TaF_7^{2-}$. The tantalum salt used as a solute in the melt could be tantalum pentafluoride $TaF_5$ or potassium heptafluorotantalate (V) $K_2TaF_7$.

### 4.3 Choice of the container materials

Construction material selection has been reviewed for fluoride melt containers[144] and cell design.[145] Only a few construction materials are entirely resistant without caution against alkaline fluoride melts at high temperature. These materials are mainly platinum group metals (e.g. Ru, Rh, Pd, Os, Ir, Pt) and their alloys, other precious metals (e.g. Au, Ag), some allotropic varieties of carbon (e.g. diamond, graphite, pyrolytic carbon, glassy carbon, etc.) and also polymorphous varieties of boron nitride (e.g. sintered, pyrolytic, cubic-borazon). It is obvious, except for graphite and glassy carbon, that the high cost of these materials prohibits their industrial use. Graphite which has been widely used as a crucible material, is not suitable for this application. Actually, its surface disintegration leads to conductive graphite flakes in the melt. Because of their low density compared with the melt, graphite flakes float and lead to short-circuits between electrodes.

Glassy carbon is more sensitive to mechanical strain during crystallization of the bath which often leads to container failure on cooling. Moreover, some common materials are suitable for handling and storing fluoride melts without moisture and oxygen. These materials are pure metals such as copper, nickel, molybdenum, or complex alloys like stainless steels, Hastelloy® X, Monel® and Inconel 600®.

Nickel could be selected advantageously. It exhibits good resistance in fluoride melts without moisture, it is easy to machine and is a cheap construction material. Thus, the crucible which has a straight form is machined by turning directly from a pure nickel bar. Wall thickness should be large to avoid creep phenomena.

### 4.4 MSE plant

A further great advantage of MSE with high quality coatings is the straightforwardness of the production plant design.[146] The basic engineering part of designing a molten salt electrolysis plant concerns (cf. Fig. 3): a nickel crucible containing the fluoride melt was introduced in a cell made from Hastelloy® X and set in the resistance furnace. The cathode can be introduced and removed from the reactor without entries of air and moisture by means of an antechamber which is closed by a large gate valve. The cell was closed by means of a water-cooled flanges set-up, the tightness was ensured by an O-ring gasket. The components of the apparatus were selected to achieve a vacuum-tight cell at high temperature. The inert atmosphere within the cell was performed by an argon stream purified by passing it through a water-oxygen trap device. Before pre-melting of the electrolyte, the reactor was purged from background contaminants by high-vacuum pumping. As the temperature reached the electrolyte's melting point the vacuum circuit was switched

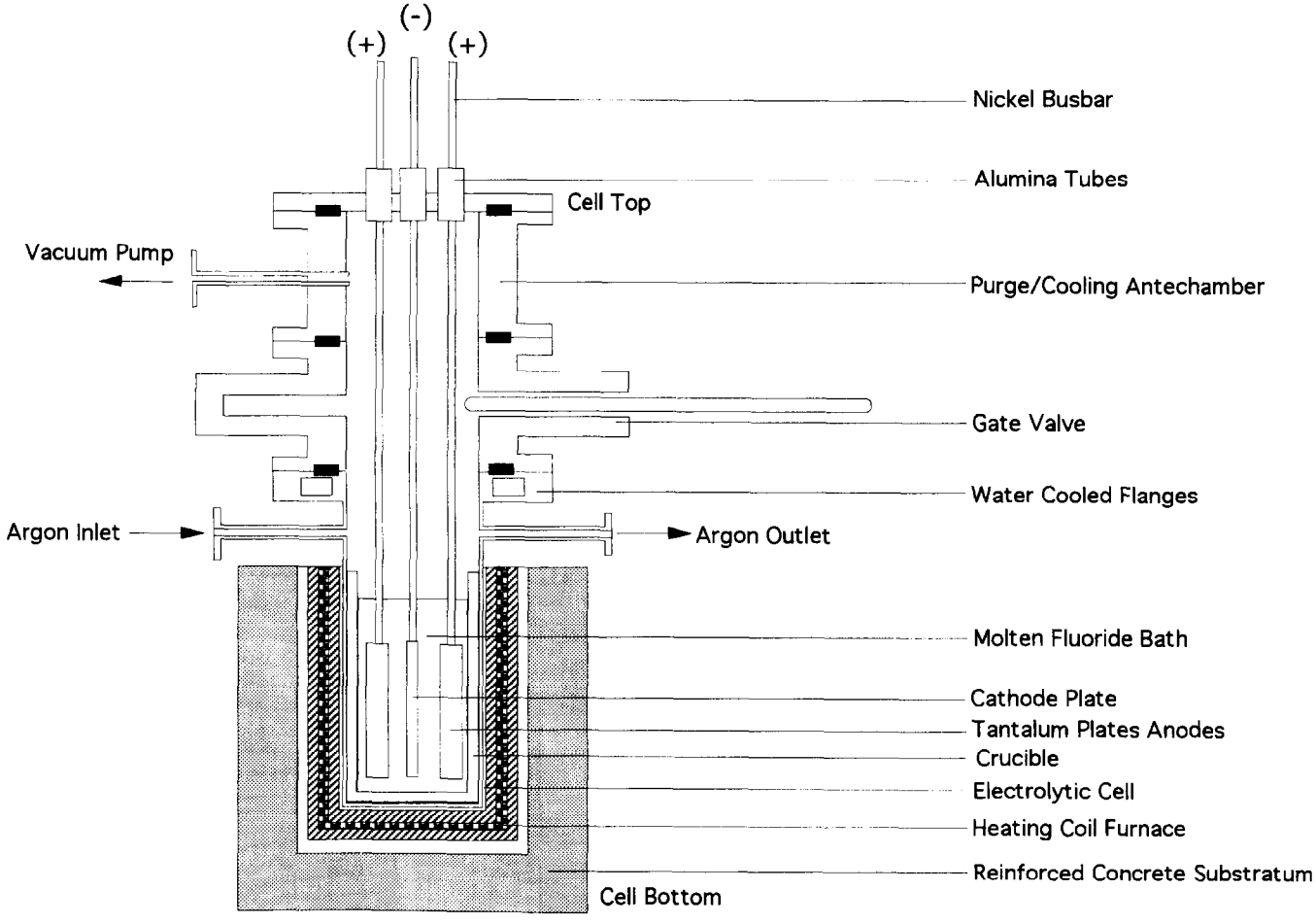



**Fig. 3.** Tantalum electroplating plant.

to a pure argon stream. The electrodes were held by nickel busbars electrically insulated from the reactor by alumina tubes. Electrical power supply was provided by an electric rectifier. Its design simplicity is equally simple whether for laboratory pilot plant or industrial plants.

## 5 CONCLUSION

In CPI, the selection of chemically inert construction material is a critical problem for engineers, especially for processes using highly corrosive chemicals. Amongst the numerous high-performance materials, it has been shown that tantalum is perfectly suited for strong corrosive acidic media under severe operating conditions owing to its tenacious protective oxide film. In these harsh environments, its corrosion rate is always below 2·54 $\mu$m/year which ensures a long service life for built-in equipment. Moreover, in addition to its chemical inertness, tantalum exhibits good mechanical, thermal and electrical properties suited to industrial applications. However, its high cost prohibits solid tantalum from being used in chemical engineering devices. Nevertheless, clad devices and vessels fabricated from thin tantalum coatings which ensures excellent protection of the base metal against corrosion, are an attractive solution. Amongst the several tantalum coating techniques described, the three main techniques which give a protective coating of tantalum against corrosion attack are: Explosion Clad (EC), Chemical Vapor Deposition (CVD) and Molten Salt Electrodeposition (MSE). Explosion clad produces a thick coating (1 mm) which leads to large amounts of metal being used. A cheap thin coating (100 $\mu$m) can therefore only be obtained with the two last techniques. By contrast with CVD, which has been developed on an industrial scale, MSE is not now widely used for tantalum clad vessel manufacturing. Nevertheless, MSE has many advantages with regard to CVD, such as the accurate control of the coating thickness by current control, the simple design of plants, the high deposition rate (100 $\mu$m/h) and good throwing power. Therefore, in the future, MSE could be an attractive alternative when manufacturing tantalum clad vessels.

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