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USE OF TITANIUM IN INDUSTRIAL CHEMISTRY AND ELECTROCHEMISTRY

Abstract:

Due to its outstanding corrosion resistance titanium has become an important material for process equipment construction.

The possible applications of titanium in the chemical industry are numerous: it is used in the construction of reaction vessels, columns, stirres, pipelines, etc. For cooling or heating corrosive media heat exchangers manufactured from this material are used, which can be designed as heating coils, bayonet heaters or as tube heat exchangers.

The classical application of titanium (activated with precious metals) in the industrial electrochemistry has been the use as a chlorine producing anode. In addition titanium has recently become an important material in cell construction.

The Use of Titanium in Industrial Chemistry and Electrochemistry

1. Introduction

Due to their outstanding corrosion resistance titanium and its alloys have become important materials for process equipment construction. Besides aerospace industry, chemical industry is the biggest consumer of this metal.

The possible applications of titanium in chemical industry are numerous: it is used in the construction of reaction vessels, columns, stirrers and pipelines. For cooling or heating corrosive media heat exchangers of this material are used, which can be designed as heating coils, bayonet heaters or as tube heat exchangers (Fig. 3-5).

Titanium components can be manufactured in self supporting construction or in combination with other metals. In many cases a lining of the carrier material is sufficient. If vacuum is applied or thermal conductivity is required, cladding has to be used. As titanium has a tendency to form intermetallic phases with iron, at high temperature explosive cladding is applied.

The classical application of titanium (activated with precious metals) in the industrial electrochemistry has been the use as a chlorine producing anode. In addition titanium has recently become an important material in cell construction (Fig. 6-7).

2. Properties of Titanium

2.1 Physical and Mechanical Properties

The commercially pure (c.p.) and alloy grades typically used in industrial service are listed in Table 1. In general alloying with palladium (TiGr.7) or nickel and molybdenum (TiGr.12) improves the corrosion resistance of c.p. titanium whereas aluminium and vanadium result in a higher strength.

In the construction of process equipment the grades 2 (c.p. Ti), 7 (TiPd) and 12 (TiNiMo) are mainly used.

When designing with titanium various physical properties have to be taken into account (Table 2). The apparatus are calculated by means of the usual design codes e.g.:

ASME - American Society of Mechanical Engineers
AD - ArbeitsausschuB flir Druckbehalter

In terms of strength titanium alloys can be compared to austenitic steels. Due to its low density of 4.5 g/cm^3 a weight saving of 42% can be achieved in comparison to steel costruction having the same mechanical data. Scales are hardly formed on titanium, which improves the beat transfer in heat exchangers although the thermal conductivity is rather low compared to steel or nickel.

The considerable thermal expansion differences between steel and titanium have to be considered. Tube heat exchangers for example are fitted with expansion joints to compensate differences in extension (Fig. 10).

2.2 Corrosion Properties of Titanium

The corrosion resistance of titanium in many aggressive media is based on the formation of a passive oxide layer on the surface. Because of this, titanium is mainly used in oxidizing media. Due to its excellent stability in chloride, chlorate and chlorine containing brines, it is used in chlor-alkali processes as a material of construction and - activated with precious metals - as a chlorine producing anode (Fig. 1-2).
Titanium is not recommended in fluorine and fluoride containing media, dry chlorine gas and red fuming nitric acid. The corrosion behaviour in non-oxidizing acids e.g. HCl and H_2SO_4 is inadequate in particular at elevated temperatures and low pH

values. There are a number of possibilities to improve the passivation behaviour in these environments. Oxidizing additive such as NBO_3 or chromate have a beneficial influence on the formation of the passive oxide layer. The free corrosion potential can also be shifted into the passive state by:

- Application of an external, anodic current.
- Electric coupling to a more precious element (e.g. Pt or Pd)
- Alloying with a more precious metal (e.g. Ti 0.15 Pd)

By alloying with palladium the susceptibility of titanium to crevice corrosion is improved. To a certain extent this is also achieved by nickel and molybdenum, applied at Ti Grade 12.

3. Applications of Titanium

3.1 Applications in the Chemical Industry

Referring to its excellent corrosion resistance in many aggressive media titanium is used in a number of chemical processes. Process equipment of any kind such as reactors, heat exchangers, piping, electrodes, etc. for the production of petrochemicals, plastics intermediate products, acetic acid, nitric acid, chlorine gas, urea, etc. are manufactured from titanium (Fig. 2). It is furthermore used in sea water desalination plants, marine applications, galvanotechnique and corrosion control.

Apparatus manufactured from solid titanium can be applied up to a maximum temperature of 250°C. In titanium lined devices the temperature should not exceed 200°C whereas titanium clad constructions ~an be used up to 500°C.

3.2 Applications in the Electrochemical Industry

The classical application of titanium, activated with precious metals or their oxides, in the industrial electrochemistry has been the use as a chlorine producing anode as a substitute material for graphite.

Apart from chlor-alkali processes titanium electrodes are applied in a number of electrolytic processes, e.g. in the generation of chlorate and hypochlorite from NaCl solutions. Membrane cells fitted with titanium anodes are applied in electroorganic synthesis. In galvanotechnique the insoluble anodes of titanium tend to replace the well known soluble anodes such as lead or graphite. Titanium anodes are furthermore used in active corrosion control such as cathodic protection (e.g. inside protection of tanks and pipelines).

More and more titanium is used for the construction and lining of cell components such as cell covers, piping or frames in membrane cells.

In brine purification Kelly Filters manufactured from titanium, admit double filter area in comparison to rubberized steel construction (Fig. 8). The double titanium frame having the same size as one single steel frame is covered with a filter mat. By doubling the filter capacity the use of titanium turned to be economic.

4. Constructing with Titanium

4.1 Welding

Normally titanium is welded by the TIG (tungsten inert gas) technique with or withouth filler metal. As titanium reacts easily to the atmosphere during welding, it has to be carried out in inert atmosphere either in protective chambers or with suitable protective equipment. The normally used Argon must have a purity of a least 99,95%.

4.2 Multi-Tube Heat Exchangers

The high corrosion resistance of titanium enables to reduce the wall thickness of tubes in comparison with those of stainless steel and copper alloy tubes. Scales are hardly formed on the heat-transfer surface, thus improving the condensation properties of the heat exchangers. For these reasons the heat transfer ratio of titanium tubes is superior to that of the other metals mentioned above.

Multi-tube heat exchangers are composed of shells, tubes, tube sheets, baffle plates, expansion joints, etc. (Fig. 9-12). In most cases only one of the flowing liquids in the heat exchanger is corrosive. It is economical to set the tube interior as the corrosive side and use titanium only for the tubes and the tube sheets. Seamless and welded titanium tubes can be used. In the recent years the application changed from seamless to welded titanium tubes. Now seamless tubes are only used if high strength is prevalent due to high pressure.

The tube ends are fixed to the tube sheets by expanding. The clearance between the tube sheet hole and the tube should be in the range of 0.1 to 0.5 mm. To achieve a better stability, grooves can be cut into the wall of the holes. The tubes are normally rolled-in with a tube expansion rate of 8 to 10%. If higher reliability is required the tubes are additionally welded to the tube sheets after rolling-in (Fig. 11).

The tube sheets are manufactured from solid titanium, titanium clad steel or may be loose lined.

4.3 Explosive Cladding

The decision whether to use a loose lining or clad material is influenced by several factors. Due to high differences in thermal expansion (e.g. titanium and stainless steel) loose linings may separate at high working temperature. Under vacuum conditions the loose lining can collapse whereas at high pressures the thermal expansion beads are depressed and can no longer function. If good thermal conductivity is required clad material has to be used because of its good heat transfer properties.

As titanium shows a tendency to form brittle intermetallic phases with iron at high temperatures explosive cladding (cold welding) has to applied.
In explosive cladding the flyer plate is placed parallel to the stationary base plate at a specified gap distance. A detonation front is established causing plate acceleration and impact of the flyer plate on the base plate surface. The impulse delivered from the flyer plate causes deformation of this plate at an angle that is equal to the dynamic collision angle β. The velocity of the collision point VC along the base plate surface is equal to the detonation velocity of the explosive VD (Fig. 13). The acceleration of the plate VP may be as high as 500 m/s. The high pressure (10 to 50 kbar) applied at the collision point results in the welding of the two materials. The bonded zone has a wave-like appearence (Fig. 14).

Generally, titanium sheets having a thickness of 2 to 4 mm are used for cladding. In designing, the computation of strength is done with regard solely to the carrier metal. Due to the fact that it is not possible to weld titanium with other materials, a special technique must be considered in construction with clad material. The titanium cladding is removed near the weld. After welding the steel, the weld is sealed by an overlapping titanium stripe welded to the explosively clad lining. Nozzles may be loose lined or carried out in solid wall construction.

4.4 Cell design

When designing with titanium as a conductor its relatively high electrical resistivity has to be taken into account (Table 2).

In cell design the conductivity of titanium often is the limiting factor in current-carrying components. Because of this, titanium lined or clad copper is used for current distributors if high electrical conductivity is required.

5. Conclusion

By using titanium as a material of construction for chemical process equipment and components of electrolytical cells a lot of highly corrosive media can be handled. As soon as the corrosive agents turn to attack titanium e.g. inorganic acids at elevated temperatures and low pH values the special metals zirconium, niobium and tantalum have to be applied.

Table 1: Chemical Composition and Mechanical Properties of some Titanium Alloys

Titanium		Chemical Composition [Weight-%]			Yield* Strength	Tensile Strength	Elongation
ASTM	DIN	Fe (max.)	O (max.)	other	[N/mm^2] (min.)	[n/mm^2]	[%] (min.)
Grade 1	3.7025	0.20	0.12		200	290–410	30
Grade 2	3.7035	0.25	0.18		270	390–540	22
Grade 3	3.7055	0.30	0.25		350	460–590	18
Grade 4	3.7065	0.35	0.35		410	540–740	16
Grade 5	3.7165	0.25	0.20	6 Al/4 V	850	$\geq$900	10
Grade 7	3.7035	0.25	0.18	0.15 Pd	270	390–540	22
Grade 12	–	0.30	0.25	0.3 Mo/0.8 Ni	370	$\geq$490	18

* at 1.0% offset

Table 2: Physical Properties of Various Materials

Material	Specific Gravity [g/cm^3]	Melting Point [°C]	Expansion Coeff. [/°C]	Thermal Conduct. [W/m°C]	Modulus of Elastity [kN/mm^2]	Yeld* Strength [N/mm^2]	Electrical Resistivity [μΩcm]
Ta-ES					172	140	
	16.6	2,997	$6.5x10^{-6}$	54			12.5
Ta-GS					180	200	
Nb	8.6	2,460	$7.2x10^{-6}$	52	107	105-140	16
Zr 702	6.5	1,845	$5.9x10^{-6}$	52	108	207	44
Ti Gr.II	4.5	1,670	$8x10^{-6}$	17	105	225	57
Mo	10.2	2,610	$5.3x10^{-6}$	142	325	600	5.2
Steel (HII)	7.9	1,530	$12x10^{-6}$	62	205	255	9.7
Staineless St	7.9	≈1,400	$17x10^{-6}$	16	200	265	72
Nickel (LC)	8.9	1.450	$15x10^{-6}$	91	205	80	9.5
Hastelloy C4	8.6	≈1,350	$11x10^{-6}$	12	195	305	130
Copper	8.9	1,080	$17x10^{-6}$	381	108	-	1.7

* minimum, at 0.2 % offset

Good Resistance	Limited Resistance	No Resistance
Oxidizing Media	Reducing Media	Fluorine
		Fluorides
Chlorides	Sulfuric Acid	Chlorine (dry)
Brine	Hydrochloric Acid	Red Fuming
Seawater	Phosphoric Acid	Nitric Acid
Chlorates		
Chlorine (moist)		
Alkalies		

increasing <——— Resistance ———> decreasing

Oxidizing Media	Reducing Media
HNO_3, CrO_4^{2-}, Fe^{3+}, Cu^{2+}	high concentration
Ti 0.2 Pd	high temperature

Fig. 1: Corrosion Resistance of Titanium

Applications	Components
Chemical Industry	Process Equipment
Petrochemistry	Reaction Vessels
Plastics Intermediate Products	Columns
Production of:	Heat Exchangers
Acetic Acid	Piping
Nitric Acid	Pumps
Urea	Valves
Fertiliser	
Electrochemistry	Cell Components
Chlor Alkali Electrolysis	Electrodes
Hypochlorite Generation	Cell Covers
Chlorate Generation	Cell Frames
Electroorganic Synthesis	Anode Baskets
Galvanotechnique	
Seawater Desalination	
Marine Applications	
Corrosion Control	

Fig. 2: Applications of Titanium

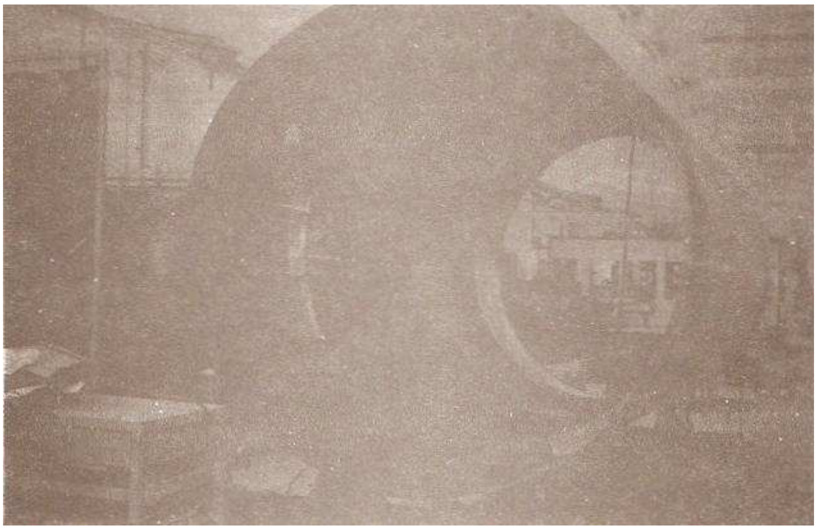

Fig. 3 – Column manufactured from solid titanium

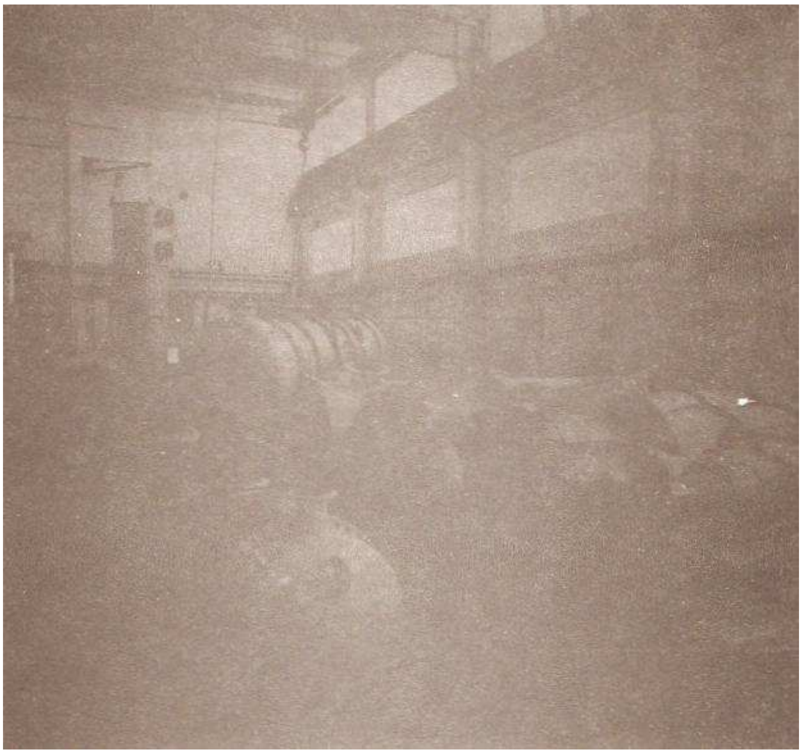

Fig. 4 – Titanium Heat Exchangers manufactured from Ti grade 2 and 12 for a salt generation plant, exchange surface: 7.5 m^2 to 532 m^2

Fig. 5
Stirrer manufactured from solid titanium

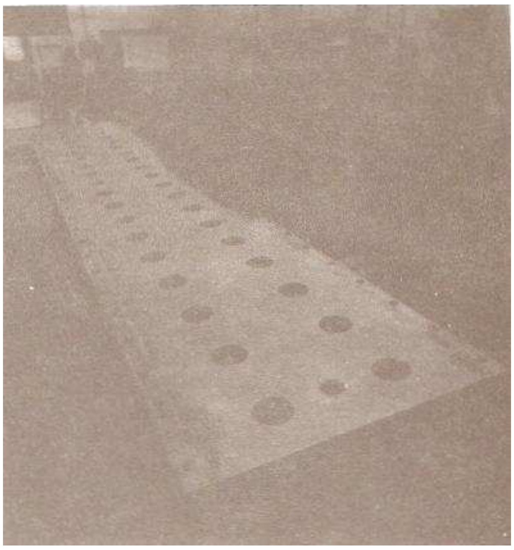

Fig. 6 Titanium lined cell cover (Mercury cell)

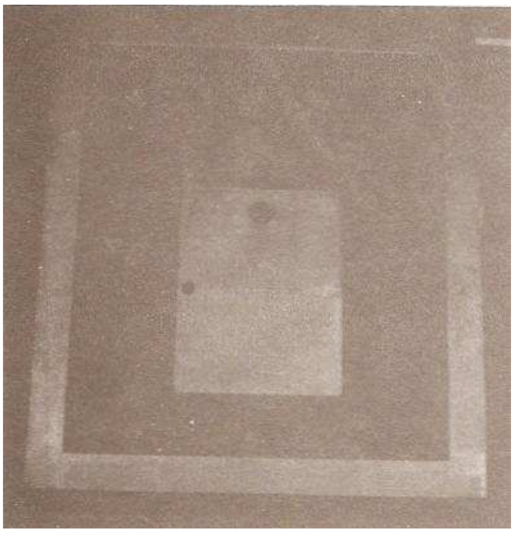

Fig. 7
Titanium cell cover (diaphgram cell)

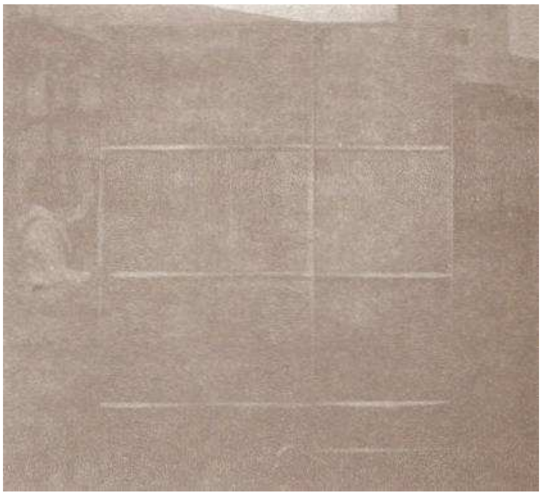

Fig. 8
Kelly Filter for brine purification manufactu-red from titanium sheet

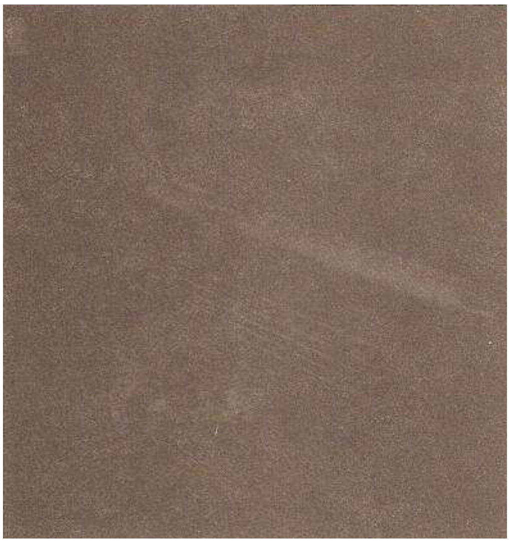

Fig. 9
U-tube Heat Exchanger,
arrangement of tubes
and baffle plates

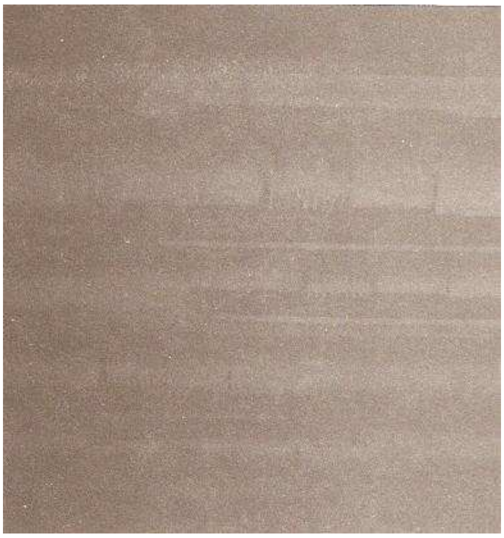

Fig. 10
Expansion joints to
compensate differences
in thermal expansion

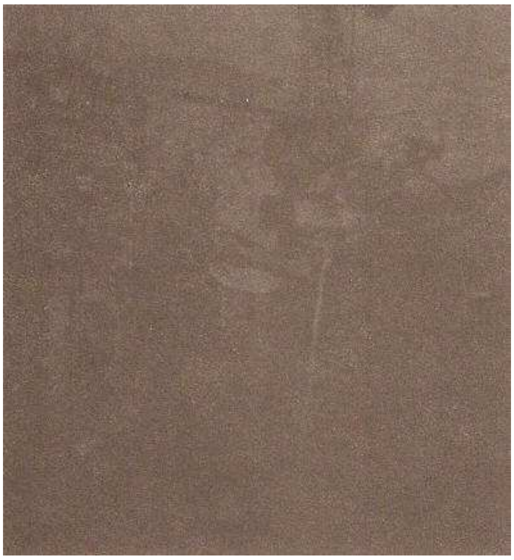

Fig. 11
Welding of tubes
to the tubes sheet

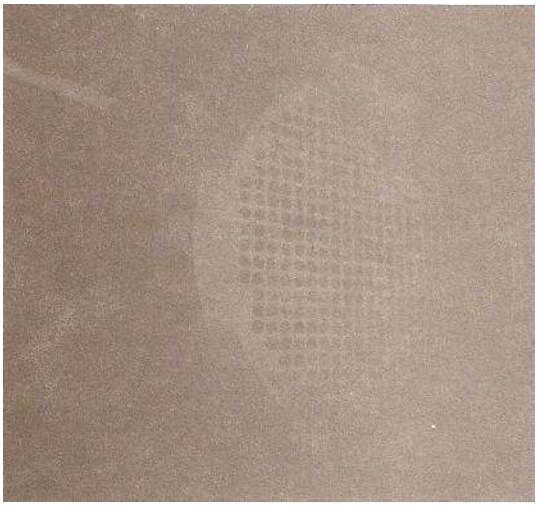

Fig. 12
Titanium Tubes Heat
Exchanger, exchange
surface 101 m2, tube
sheets explosively clad
with Ti 0.2 Pd

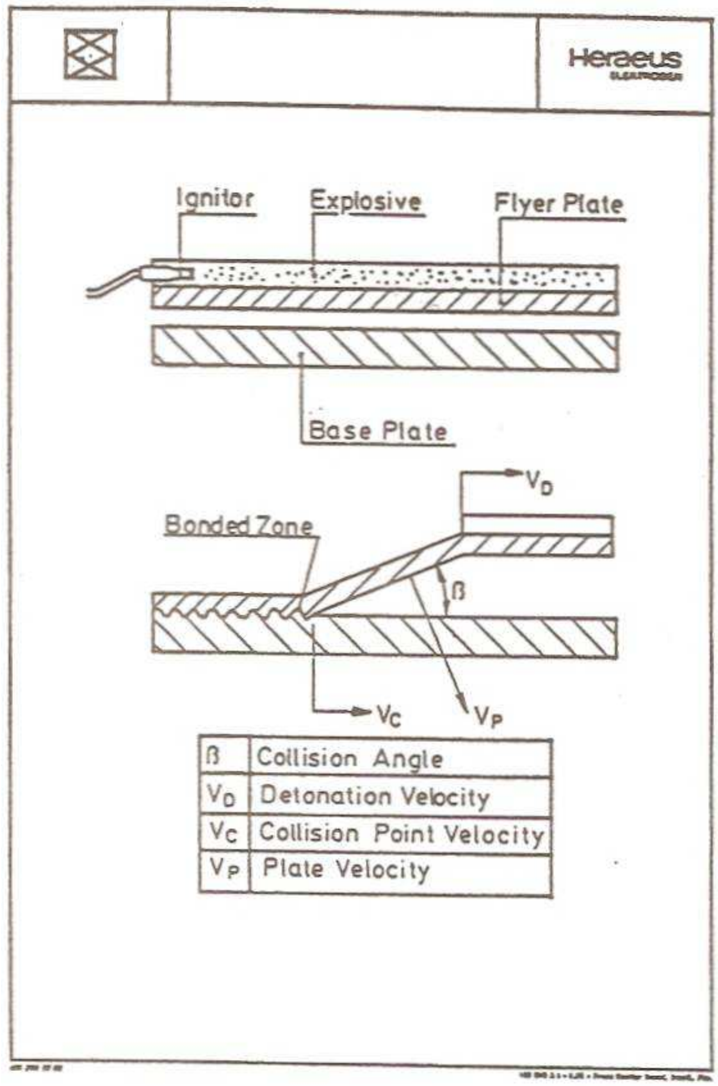

Fig. 13
Arrangement and procedure of explosive cladding

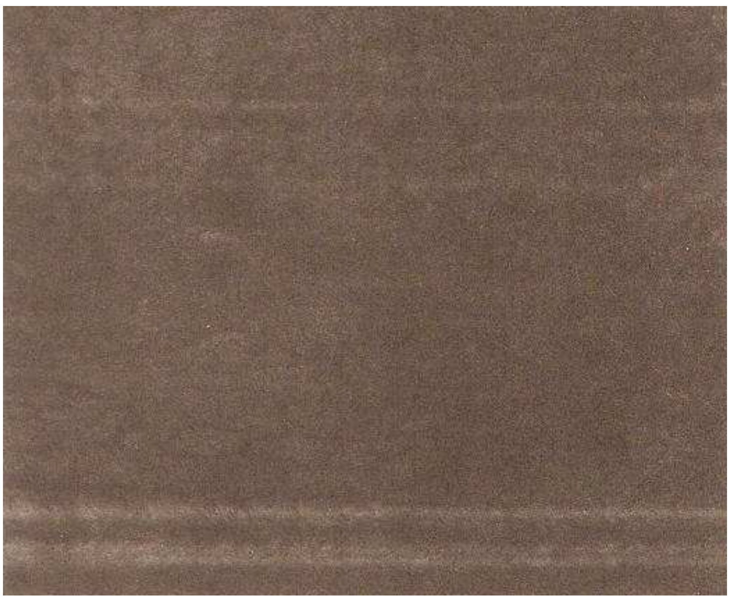

Fig. 14
Bonded zone of explosively clad material
(cross section)

6. References

1. K. Rudinger: Sonderwerkstoffe fur den Korrosions-schutz; in Kontakt & Studium Bd. 64, Expert-Verlag, Grafenau/Wurttemberg, FRG, 1981.

2. K. Rudinger: Titan und Titanlegierungen; Z. Werkstofftech. 9, 1978, p. 181.

3. Titanium and Titanium Alloy, Daido Steel Co., Nagoyu, Japan, 1985.

4. Titanium Zirkonium, Nippon Mining Co., Tokyo, Japan.

5. Titanium Tikrutan, Schmiedewerke Krupp-Klocknel GmbH, FRG.

6. Titan und Titanlegierung, Tisto GmbH, Dusseldorf, FRG.

7. Corrosion Resistance of Titanium, Timet Division Pittsburgh, Pennsylvania, USA.

8. TiCode 12, Timet Division, Pittsburgh, Pennsylvania, USA.

9. Corrosion Resistance of Titanium, IMI Titanium, Birmingham, GB.

10. Ch. Liesner: The special metals Tantalum, Titanium and Zirkonium in chemical engineering plant; special edition of W.C. Heraeus GmbH, Hanau, FRG, 1978.

11. F. Sperner: Die reaktiven Metalle Ti, Zr, Hf, V, Nb und Ta, Technologie und Einsatzgebiete; Werkstoffe und ihre Veredelung, 2 (6) (1980), p. 291.

12. F. Schreiber: Sondermetalle in der chemishen Verfahrenstechnik; Chemie-Technik, 10 (1981), p. 203.

13. D.F. Lupton, L. Amend, H. Heinke, F. Schreiber: The use of special metals in highly corrosion resistant chemical plant; special edition of W.C. Heraeus GmbH, Hanau, FRG, 1982.

14. R. Brandner: Reaktoren aus Sondermetall; Chemie-Technik, 12 (2) (1983), p. 72.

15. D. Wall: Modern Chlor-Alkali Technology, Soc. of Chem. Ind., London, 1986.

16. Industrial Electrochemistry, editor: D. Pletscher, Chapman and Hall, London/New York, 1982.