FIFTH INTERNATIONAL MEETING ON TITANIUM

APPLICATIONS FOR CAST TITANIUM COMPONENTS IN THE PROCESS INDUSTRY

By :-

T J Glover B. Sc. M. I. Corr.Sc. T
Inco Engineered Products Limited
Birmingham, U.K.

INTRODUCTION

Over the past twenty years there has been a steady growth in the utilisation of wrought titanium in Europe to resolve corrosion problems in the more aggressive environments encountered in the process industry - in particular fabricated heat exchangers and pressure vessels are commonplace. This growth has not been mirrored in the use of cast components for pumps, valves and other ancillary equipment which are required to complete the package. The reason for this can be attributed to a combination of factors including high prices, availability, variable casting integrity and lack of technical publicity to design engineers.

In fact availability has been a major factor particularly with regard to large components as, until five years ago, the largest casting available was 80-90kg with maximum dimensions of 900 x 900 x 750mm. This deficiency has to some extent been overcome. by the commissioning in 1983 of a new foundry in Charleroi, Belgium with a 1000kg pour capacity. This foundry enables Europe to compete on an equal basis in a market previously dominated by the USA. After the skull, gating and rising systems have been accounted for the maximum single casting weight that can be achieved is about 500kg.

This substantial increase in casting size enables centrifugal and axial pumps and hall and butterfly valves to be manufactured which can operate in up to 24" (600mm) diameter piping systems. The use of vacuum melting, centrifugal pouring and hot isostatic pressing ensures the production of castings which have a high external and internal integrity.

PHYSICAL PROPERTIES

Whilst there is a wide range of wrought titanium alloys available there is only need to consider three for use as castings in the process industries. Their chemical compositions are given in Table l.

Table 1

Grade	C3	C5	C7B
Nitrogen	0.5	0.5	0.5
Carbon	0.1	0.1	0.1
Hydrogen	0.015	0.015	0.015
Iron	0.25	0.40	0.20
Oxygen	0.40	0.25	0.40
Aluminium		5.5-6.75	
Vanadium		3.5-4.5	
Palladium			0.15

Grade C3 is the most common grade of the commercially pure (CP) range and has similar mechanical properties to Grade C7B, the palladium containing alloy which has been developed to improve the resistance of titanium to reducing environments. Grade C5 has similar corrosion resistance to the CP grade but is substantially stronger as shown in Table 2.

Table 2

Grade		C3	C5	C7B
Yield Strength (MPA)				
	MIN.	380	825	275
	TYPICAL	445	890	-
Tensile Strength (MPA)				
	MIN.	450	895	345
	TYPICAL	550	1040	-
Elongation (%)	MIN.	12	6	15
	TYPICAL	18	10	-
Typical Hardness (BHN)		230	320	-

Grade 5 is often specified for balls for valves and pump impellers where erosion and abrasion conditions are encountered. Cast components have similar strengths to their wrought equivalents but do tend to have slightly lower ductilities. The impact strength of Grade C5 at 26J is again equivalent to the wrought equivalent and only in its fatigue resistance is the cast alloy inferior to the wrought material.

Titanium is a light material having a density 60% that of steel so that its strength to weight ratio is highly attractive when compared with other corrosion resistant alloys particularly when the Grade C5 is used. This is well illustrated in Table 3.

Table 3

Material	Yield Strength at 20°C N/MM^2	Density G/CM^3	Strength Density Ratio	Relative to Grade 2Ti	Relative to Grade 2Ti
Titanium 2	275	4.51	61	100	32
Titanium 5	830	4.42	188	308	100
Type 316 Stainless Steel	230	7.94	29	48	15
254 SMO	300	8.00	38	62	20
2205 Duplex	450	7.80	58	95	31
Monel400	175	8.83	20	32	11
Inconel 625	415	8.44	49	80	26
Hastelloy C-276	355	8.89	40	66	21
70/30 Copper Nickel	120	8.90	13	21	7

On a practical level, availability for Grades 3 and 5 does not pose a problem as these alloys are melted on a daily basis. For Grade 7B however, where demand is comparatively low and a minimum quantity of metal for a melt is required deliveries can be longer than for the more commonly specified alloys.

CASTING TECHNIQUES

There are three major problems in the production of titanium castings:

a) High melting point of the metal and its alloys - greater than 1700°C.

b) Low fluidity of the metal at pouring temperatures.

c) High reactivity with almost all gases and solids at temperatures above 500°C.

These problems have now been overcome by:

i) Vacuum melting plus evacuation of the feeding and gating systems and the mould cavities.

ii) Centrifugal pouring.

iii) Rammed graphite sand moulds with suitable binders and coatings.

Normally titanium in the form of consumable electrode is arc melted in a vacuum. The melting crucible is a double walled copper container with water cooling which causes a solid skull of titanium to be formed on the inner surface. This skull and the absence of an atmosphere protects the molten metal from contamination. When the electrode has been consumed the metal must reach the moulds as quickly as possible. This is achieved by the use of a centrifugal pouring arrangement which is shown. schematically in Figure l.

The moulds are placed on the outer edge of a circular table of 3m diameter which, when rotating, generates a centrifugal force of 60g at the periphery. This force ensures a rapid transfer of the molten metal into the moulds and provides extra pressure for feeding during solidification thereby minimising porosity. With the use of centrifugal pouring, careful attention to the size and positioning of gating (larger gates than stainless steel are required) and good mould coatings, castings having excellent internal and external integrity can be produced which are comparable in appearance with more commonly cast materials.

The majority of commercial castings are produced in rammed graphite moulds with a surface finish of about 6μm. However, if sufficiently large quantities are required or suitable waxes exist, then an investment casting route can be used resulting in a superior surface finish of 3μm and casting with tighter tolerances requiring minimal finish machining. The maximum casting weight by this route is 90kg.

The conventional non-destructive inspection methods of radiography and fluorescent penetrant are readily applicable to titanium castings to ensure internal and external integrity.

Whilst the vast majority of commercial castings have adequate soundness, for critical components where fatigue is a critical factor, then hot isostatic pressing (hipping) should be applied to the casting which removes internal voids (microporosity). A temperature of 900°C with a pressure of 100MPA for 2 hours in a pure argon atmosphere is a typical treatment of 2h at 750°C.

The effect on mechanical properties is shown in Table 4 where there is a significant increase in ductility after the hipping treatment.

Table 4

Condition on	0.2% Yield (MPA)	UTS (MPA)	Elongation %
As cast	890	1065	8.5
HIP + Heat Treatment	890	1015	10.5

The number and length of pores present on a casting of 25mm thick section falls dramatically on hipping as shown in Table 5.

Table 5

Condition	Surface Area (μm)	Length (μm^2)
As cast	4519	63
As cast + HIP	152	16

The largest titanium melting unit in Europe has a 1 tonne capacity which, when the rising, running and gating systems have been accounted for, can produce a single piece casting of 500kg (with the low density of titanium this equates to a casting of about 1 tonne in stainless steel). The maximum dimensions are 2600 x 900 x 800mm. The largest titanium casting (385kg) produced in Europe to date was a cylinder for a bleach plant drum filter.

The maximum casting weight would be adequate to produce pumps and valves which could be installed in pipelines up to at least 500mm diameter. Ball valves, having solid titanium balls up to 600mm diameter, have been widely used in US submarine sea water systems for many years. Butterfly valves, with titanium discs up to 200mm, are currently readily available and there is no design or capacity restraint to prevent the production of such valves up to 600mm diameter.

Axial and centrifugal pumps, with a suction diameter of up to 500mm can be obtained from at least 10 pump manufacturers in Europe who have the requisite expertise in handling titanium.

Conventional metal or wooden patterns used for the production of alloys such as stainless steel can also be used for titanium with some modification of the gates and risers.

MACHINING

Titanium has a reputation as a material which is difficult to machine. This is unfounded provided that cutting tools and machining conditions are correctly selected. The main points to recognise are:

a) Cutting speeds should be about half that for stainless steel and deeper cuts should be taken.

b) Maintain a plentiful supply of cutting oil to act as both a lubricant and coolant.

c) Keep the cutting resistance to a minimum by maintaining sharp tools at the proper cutting angles. Conventional high speed steels and tungsten carbide tools are used and there is a wealth of detailed information on feeds, speeds and angles in the literature.

d) Prevent vibration by using large rigid machines.

For comparison, on taking a 6-8mm cut the following turning speeds can be achieved:

Table 6

	ft/min
Titanium Grade 3	200
Titanium Grade 5	175
Inconel 625	110
316 Stainless Steel	300

The machining costs for titanium are estimated to be about 25% more expensive than austenitic stainless steel.

WELDING

Then welding titanium it is essential to exclude air as titanium readily absorbs oxygen and nitrogen leading to hardening and embrittlement. In the event of significant porosity being present in the casting then it would immediately be scrapped but minor surface defects would be weld repaired at the foundry using a glove box chamber which, after evacuation of air, is filled with argon.

If porosity is revealed on machining and weld repair is considered to be the best course of remedial action, then this is best carried out using conventional MIG or TIG welding using a triple argon gas shield. It is necessary to shield the part after solidification of the weld bead until the metal temperature falls below 300°C. The quality of the weld can be judged by its colour - if the colour is silver or even light yellow, then shielding has been adequate. A blue/purple colouration indicates inadequate shielding.

COST CONSIDERATION

The decision on whether to use a casting as a unit of construction in process plant equipment depends on the complexity of shape and the numbers required. The cost of the pattern required to produce the casting is a significant factor in the financial equation, particularly when small quantities are required. The cost of a wooden pattern for the components required to construct pumps and valves is rarely more than twice the unit casting cost. For simple shapes and small quantities it is often more economical in time and money to machine from solid feedstock but if the components have any significant contours and cavities, then the use of a casting can be more readily justified. Obviously the larger the quantity then the easier is the decision.

Metal tools for the production of investment castings are substantially more expensive than wooden patterns for rammed graphite castings and consequently greater numbers are required to justify initial tooling costs. The use of precision investment castings reduces machining cost to about 5% of total component cost compared to up to 80% for the same components machined from a forging or billet. Whilst there is a market for machining swarf, prices are low and financial recoupment of metal costs through their sale is minimal.
Typically for 200 off the unit cost for a component machined from a titanium block was £430 compared with £130 for an investment casting.

Titanium has the image of being an expensive material of construction largely due to its association with the aerospace industry and the massive short term price rise in 1980 due to supply/demand imbalance. However, as the fourth most abundant metal on the earth's surface and a current ingot capacity of 80,000 t.p.a. supplying a 50,000 t.p.a. market, this is a gross misconception, particularly when the low density of the metal is included in the calculation. Comparative prices for large pump castings indicate that titanium is less than 3 times the price of 316 stainless steel and cheaper than high nickel alloys without adding the nickel surcharges currently being applied:

Table 7

	Cast Pump Casing (£)	Casting Wt. (kg)
Titanium	4360	130
316 Stainless St.	1685	228
Inconel 625	6130	244
Monel 400	4270	255
Hastelloy C4	6200	251

Corrosion Resistance

Titanium and its alloys have outstanding corrosion resistance but, as with all materials, its resistance is selective and care should be taken to examine the environment in detail before making a decision - these materials do not solve every corrosion problem.

Unalloyed titanium depends for its corrosion resistance on the oxide film which forms on its surface and is therefore particularly suited to oxidising environments such as nitric and chromic acids and aqueous solutions containing chlorine. Chlorine containing environments are extremely aggressive towards most materials of construction and, as a result, titanium is now the recognised metal for use in caustic/chlorine plants for handling spent brines and a wide range of chlorine containing solutions. Titanium has an equally good resistance to pitting resistance in chloride containing environments including sea water.

Reducing acids such as hydrochloric, sulphuric and phosphoric will corrode unalloyed titanium, the rate depending upon temperature and concentration and would, for practical purposes, rule out its use in such environments as other, often less expensive, materials could provide a superior service life. The corrosion resistance of titanium can however be markedly improved by the addition of 0.2% palladium to produce the grade 7 alloy. There is of course a cost penalty and grade 7 can be between 50-100% more expensive than CP grade, depending upon form and quantity required. The areas where grades 3 and 7 titanium can be used are illustrated schematically in Figure 2.

Over the years, by process of trial and error, laboratory and inplant corrosion testing and a careful examination of cost/life ratios niches have been found in the process industries where titanium and its alloys are now the optimum selection.

Hydrochloric Acid

Hydrochloric acid is extremely aggressive even at low concentrations to stainless steels and most of the high nickel alloys except for the high molybdenum grades of Hastelloys. C.P. titanium can be used up to 10% concentration and up to 38°C while the addition of palladium increases the temperature range to boiling point at the same concentration. The safe ranges of use are shown in the isocorrosion chart - Figure 3.

Nitric Acid

C.P. titanium has been extensively used for handling nitric acids where stainless steels have exhibited significant attack often intergranular in nature. Titanium offers excellent resistance over the full concentration range at temperatures up to 80°C.

Wet Chlorine

Titanium is basically the only engineering material which is unattacked by wet chlorine and related chemicals such as hypochlorites and chlorine dioxide even at elevated temperatures. This has led to its widespread use in :

(a) Manufacture of chlorine

(b) Manufacture of ethylenedichloride as an intermediate in PVC production

(c) Bleaching of pulp in the paper industry.

(d) Equipment to handle sodium hypochlorite used to prevent growth of marine biofouling in sea water systems.

Titanium is now a standard material of construction for pumps and valves in bleach plants in both North America and Scandinavia.

Pulp bleaching plants particularly the C and D stages can be extremely aggressive environments towards the conventional materials of construction such as the 316 and 317 grades of stainless steel due to the combination of low pH, high chloride ion concentrations and oxidising conditions due to the presence of active chlorine. These aggressive conditions are currently being accentuated due to the recycling of liquors to comply with environmental restrictions preventing discharge into waterways. The recycling results in an increase in chloride levels and acidity.

To overcome pitting and crevice corrosion of the stainless steel equipment, alloys with higher chromium, molybdenum and nitrogen contents such as 254SMO have been developed which offer substantial improvements. However, in the most severe cases even the superaustenitic stainless steels suffer some attack and there is a need to resort to the high performance materials such as the high nickel alloys (Inconel 625 and Hastelloy C-276) or Titanium.

Through information received from questionnaires to 45 Swedish pulp bleaching plants on material performance in service and spool tests JERNKONTORET1 established that the only alloys not attacked by corrosion were Hastelloy C-276 and titanium grades 2 and 7.

In more recent trials[2] in the USA and Canada a test spool programme was carried out comparing 24 stainless steel and nickel base alloys with two titanium alloys in 38 different bleach plant environments. The most aggressive environments encountered had pH values as low as 1.4 and chloride levels of 5500 p.p.m. operating at temperatures of 70°C. On the exposed surfaces the ranking for pitting resistance of the more commonly encountered alloys is given in Table 8 :

<u>Table 8</u>

Rank	Alloy	Total Pitting Depth (mil)
l	Hastelloy G	Nil
l	Inconel 625	Nil
l	Hastelloy C 276	Nil
l	Titanium Grade 2	Nil
11	254 SMO	86
17	904L	250
19	Incoloy 825	311
23	317L Stainless Steel	690
25	316L Stainless Steel	1158

It can be seen that the high nickel alloys and titanium were unattacked and the ranking order for the stainless steel was in accord with the levels of alloying elements added to improve pitting resistance (chromium, molybdenum and nitrogen).

In the more severe conditions under the Teflon washers on the test spools the ranking order was similar but only titanium remained free tram pitting in all of the locations :

<u>Table 9</u>

Rank	Alloy	Total Pitting Depth (mil)
1	Titanium Grade 2	Nil
2	Hastelloy C-276	l
3	Inconel 625	20
5	Hastelloy G	30
12	254 SMO	111.5
14	Incoloy 825	171
19	904L	223
22	317L Stainless Steel	288
25	316L Stainless Steel	415

Sea Water

Sea water is more corrosive than would be anticipated, particularly in crevice conditions of elevated temperatures. Of the materials commonly in marine environments only Inconel 625 and Hastelloy C have exhibited long-term immunity to attack. While some of the recently developed superaustenitic and second generation duplex stainless steels appear promising, no long-term data exists.

Titanium however after 18 years continuous exposure to quiescent ambient sea water suffered no corrosion attack, the only observed effect was a slight discolouration - no pitting corrosion was encountered.

Stagnant conditions and the presence of pollutants such as hydrogen sulphide and ammonia have no deleterious effects on the corrosion resistance.

Titanium is immune from erosion and impingement attack in sea water flowing at high velocities - its critical velocity beyond which the protective film is removed is 27 m/sec, well in excess of any velocities liable to be encountered in conventional sea water piping systems.

The introduction of abrasive sand particles to the sea water at velocities of 6 m/sec had no accelerating effect on the corrosion rate.

CP titanium is not susceptible to stress corrosion cracking in sea water. Care should be taken with the grade 5 alloy (Ti 6Al 4V) when sharp notches are present in the component as accelerated crack propogation has been observed. However, in practice, where this alloy has been commonly used for balls in valves and as impellers in pumps, to take advantage of its higher strength and hardness, no problems with cast components have been encountered.

Titanium is prone to biofouling but the attachment of marine organisms does not lead to the incidence of microbiologically induced corrosion. Fouling can be prevented by the use of continuous dosing with 0.5 p.p.m. of sodium hypochlorite or chlorine - if intermittent shock dosing with much higher levels are employed there is still no danger of corrosion as the material is highly resistant to wet chlorine solutions.

Ideally the sea water systems should be built completely in titanium to eliminate the possibility of galvanic corrosion as titanium is one of the most noble metals in the galvanic series. If however it is unavoidable to have a mixed metal system, care should be taken to ensure that anode/cathode ratios are not excessive and that large surface areas of titanium in direct electrical contact with less noble materials such as ferrous or copper base materials are painted.

CP titanium is not susceptible to crevice corrosion attack in sea water below 93°C.

The use of wrought titanium for tubes in coastal power station condensers and plates in plate-type exchangers on offshore platforms is now commonplace to handle sea water corrosion. In contrast the use of cast titanium components for sea water applications is minimal in Europe, although the use of titanium sea water ballast systems on offshore platforms in the Norwegian sector of the North Sea could soon change this material selection philosophy. On the other hand, the use of cast titanium in marine environments in the U.S.A. is widespread and the Navy in particular are using large quantities as balls for ball valves up to 24" diameter in submarines and 675 fire pumps for the surface fleet have already been ordered.

Case Histories and Service Experience

1. Nylon Manufacture

In the manufacture of terephthalic acid, an intermediate in nylon production, extremely aggressive conditions exist in the reactor stage where 98% acetic acid at 240°C and a pressure of 400 p.s.i. contaminated with 0.1% of the bromide catalyst has to be handled. Corrosion tests carried out in simulated laboratory conditions resulted in corrosion rates of 0.01-0.1mm/year for C.P. titanium compared with 1-10mm for Hastelloy C, the alternative material selection. Observations of cast titanium in the plant indicate a corrosion rate of 0.1mm/year. 3" diameter titanium ball valves installed 8 years ago are still in service and showing no signs of requiring replacement.

2. Sea Water

A titanium pump has been running virtually continuously since December 1965 at the LaQue Corrosion Centre pumping water from the sea through the troughs containing corrosion test specimens. The pump is a single stage centrifugal pump operating at 3500 R.P.M. typically delivering 600 G.P.M.

3. Caustic/Chlorine Production

(a) Chlorine Absorption

A centrifugal titanium pump weighing about 90kg with a 250mm suction, 200mm discharge and 425mm casing/impeller size was installed in 1981 to handle 12% sodium hydroxide, 10% sodium hypochlorite and 8% sodium chloride at 80°C. The pump is still operating and, except for seal changes, no problems have been encountered and no corrosion observed.

(b) Chlorine Treatment

A small titanium centrifugal pump of 100mm suction, 75mm discharge with a 250mm impeller was installed in 1980 and has operated continuously since, pumping chilled water at 16°C, which is saturated with chlorine.

4. Brine Transfer

Two centrifugal pumps, having 200mm suction, 150mm discharge, with a 350mm impeller, were installed in 1972 to handle 22% brine saturated with chlorine at 75°C and are still operating satisfactorily.

All of these pumps referred to in the caustic/chlorine plants were supplied by Durco.

5. Caustic/Chlorine Plant

In 1978 5 small titanium pumps were installed in Germany to handle chlorinated brine ÷ 10% solids with particles up to 10mm diameter at 80°C - they are still performing perfectly after 10 years in service. The pumps, with a capacity of $30m^3/h$ and a head of 38m had a suction diameter of 80mm with a discharge of 65mm and were manufactured by Eggel-Turo of Switzerland.

6. Steel Picklinq Plant

In 1975 Ochsner of Austria installed titanium pumps in a local steel works to handle hydrochloric acid pickling solutions at elevated temperatures. These are still operating.

7. Bleach Solutions

Titanium was first used[3] in bleach plants in 1955 when a 3mm liner was fitted into a chlorine dioxide mixer. After 10 years in service it had given twice the life of that which would have been obtained using 12mm thick Hastelloy C.

Titanium was used much later in Europe and it was not until 1980 that Sunds Defibrater[4] used the metal to construct bleach plant filter drums. A cost comparison showed that a titanium filter drum cost more than twice that of conventional 316L stainless steel to fabricate :

Table 10

Material	Cost Factor
316L Stainless Steel	0.8
3l7L Stainless Steel	1
254 SMO	1.3
Titanium	1.8

However, from past experience of stainless steel performance and a consideration of spool test data it is highly probable that the increased initial investment cost will be more than compensated.

Titanium pumps are becoming a standard component for handling chlorine dioxide liquors in bleach plants and scanpump of Sweden alone have supplied more than 100 pumps between 1980 and 1982 all of which are still operating without any significant deterioration due to corrosion. The sizes range from a capacity of $10m^3/h$ with a 10m head (50mm inlet/40mm outlet with a l60mm impeller) to $120m^3/h$ with a 50m head (150mm inlet/125mm outlet with a 400mm impeller).

Ingersoll-Rand, IMPCO division Nashua, NH have been supplying titanium cylinders for vacuum filters since 1963 and now have 62 such installations throughout the world. These are all fabricated structures from wrought materials but castings are used in their mixers which homogenise the gaseous chemical and the pulp slurry. Since 1985 seventeen mixers each weighing 3100 lbs have been installed in US mills all handling chlorine dioxide.

Conclusions

It can be seen from laboratory data and case histories that, provided careful consideration is given to the precise environment to be handled, titanium and its alloys can provide cost effective answers to the most aggressive chemical environments.

Whilst size is still limited compared with conventional stainless steels, this new foundry gives an added dimension to the European availability of large titanium castings for process plant construction particularly for pumps and valves.

REFERENCES

1. Wallen B. ‘Stainless Steel and Titanium Corrosion in Bleach Plants’ 7th Int. Scandinavian Corrosion Congress 1975. pp 591-609

2. Tuthill A.H. ‘Resistance of Highly Alloyed Materials and Titanium to Localised Corrosion in Bleach Plant Environments’ Materials Performance, Sept. 1985 pp 43-49

3. Field C.W. ‘The Use of Titanium in the Pulp and Paper Industry’. Materials Protection Oct. 1966 pp 47-48

4. B. Ljung. ‘Experiences of Titanium Filters in Bleach Plants’ 4th Int. Symposium of Pulp & Paper Industry Stockholm June 1983 pp 149-152

FIGURE 1

CENTRIFUGAL CASTING

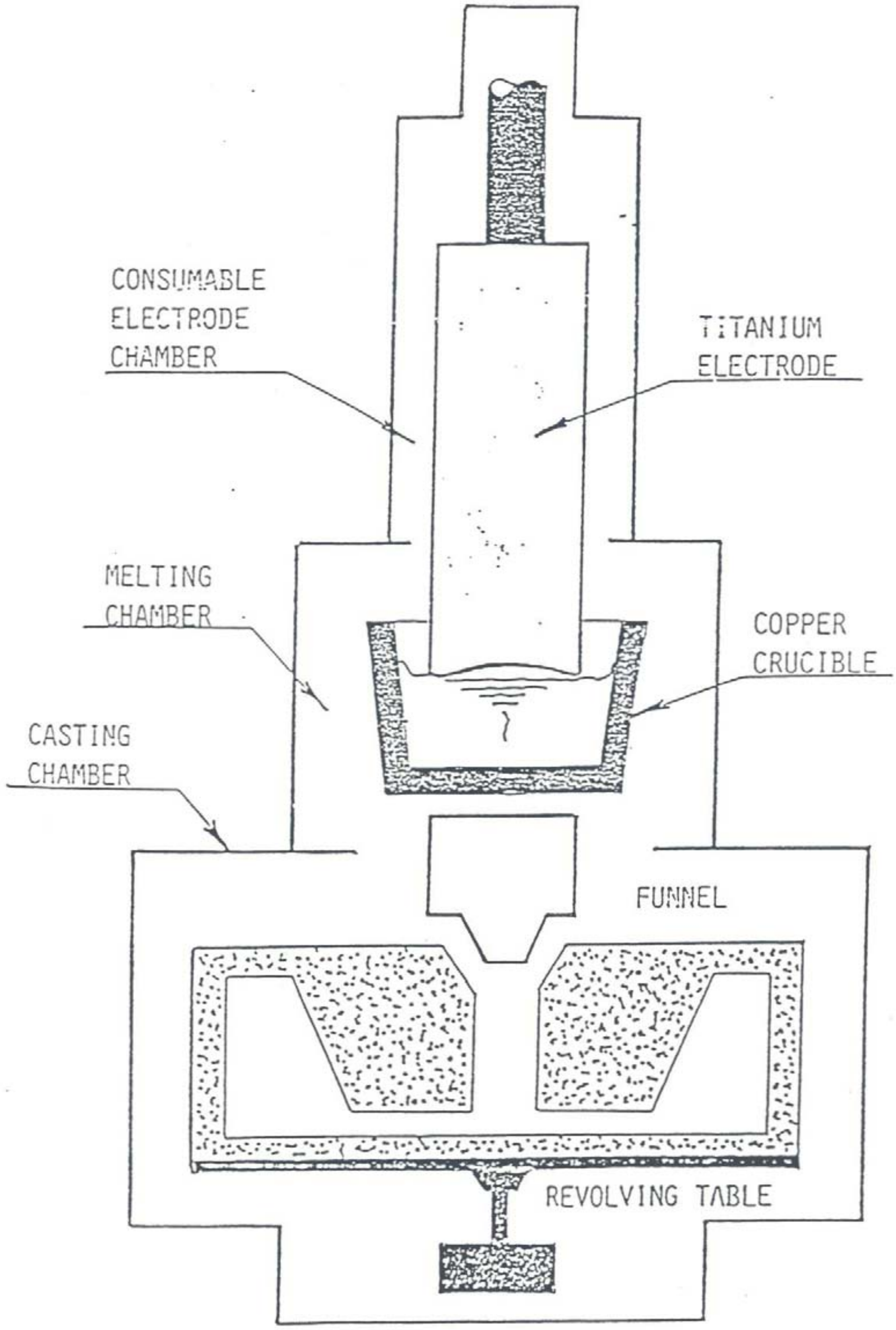


FIGURE 2

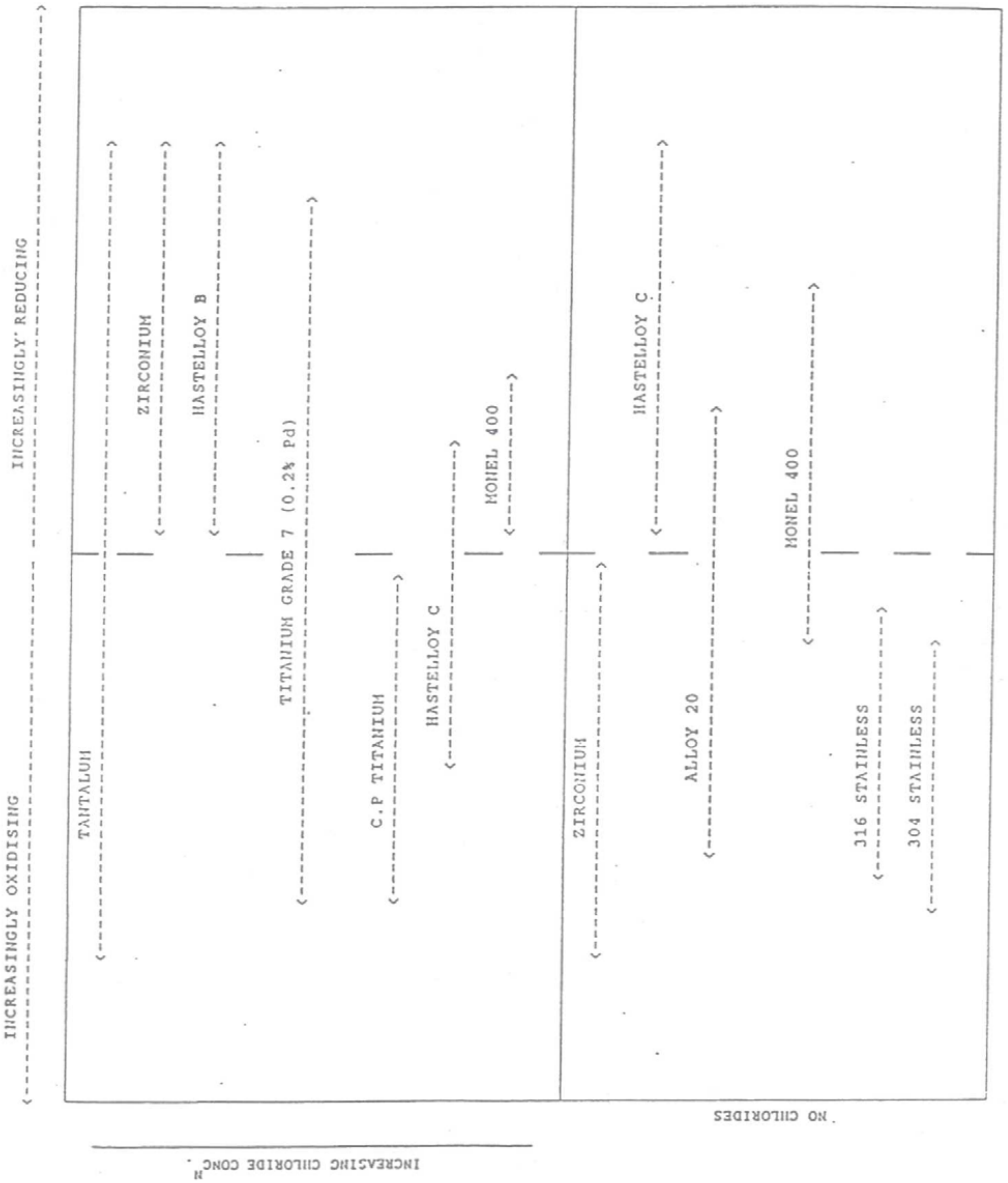
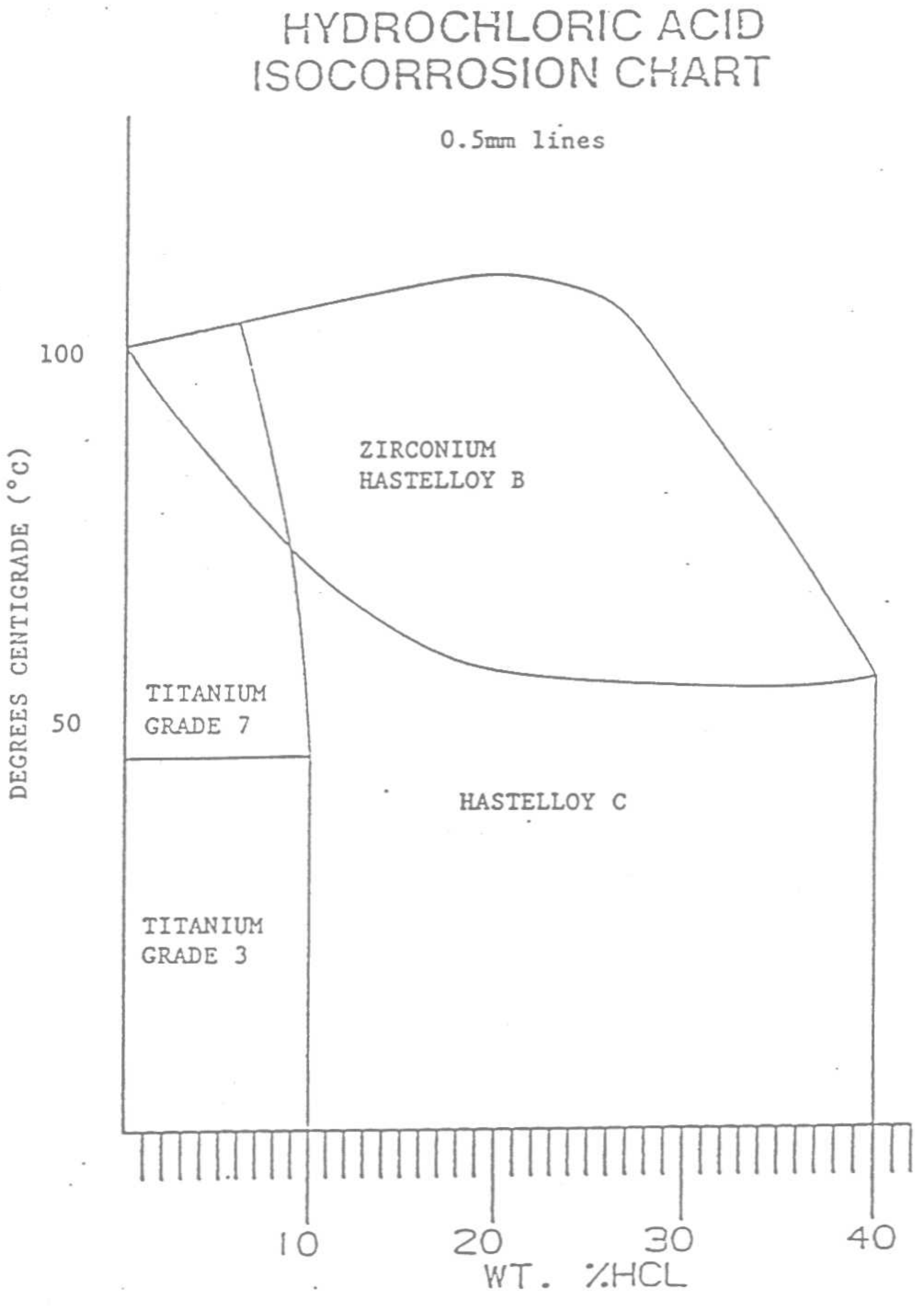

INCREASINGLY REDUCING
INCREASINGLY OXIDISING
TANTALUM
ZIRCONIUM
HASTELLOY B
TITANIUM GRADE 7 (0.2% Pd)
C.P TITANIUM
HASTELLOY C
MONEL 400
ZIRCONIUM
HASTELLOY C
ALLOY 20
MONEL 400
316 STAINLESS
304 STAINLESS
SCHEMATIC CORROSION CHART
NO CHLORIDES
INCREASING CHLORIDE CONCN

FIGURE 3


HYDROCHLORIC ACID
ISOCORROSION CHART
0.5mm lines
DEGREES CENTIGRADE (°C)
100
50
ZIRCONIUM
HASTELLOY B
TITANIUM
GRADE 7
HASTELLOY C
TITANIUM
GRADE 3
10
20
30
40
WT. %HCL