IV MEETING SUL TITANIO

Organizzato dalla GTT

17 Novembre 1988

Sala dei 500

Unione Industriale, Torino

GTT

GINATTA TORINO TITANIUM

INTERVENTI

POSTERS

Marco V. Ginatta

GTT

INAUGURAZIONE DEL IV MEETING SUL TITANIO

Desideriamo dare un cordiale benvenuto a tutti i partecipanti a questo IV convegno sul titanio.

Io sono Marco Ginatta ed oggi sarò il conduttore di questo incontro durante il quale, come avete visto dal programma, molti eccellenti specialisti ci parleranno dei vari aspetti tecnico-economici del titanio.

Ricordo brevemente, per coloro i quali non avessero partecipato ai convegni degli scorsi anni, che la caratteristica di questo incontro, l'obiettivo principale del nostro convegno di oggi è la divulgazione di informazioni riguardanti il titanio nel modo più adatto ad essere accolto da parte di operatori industriali in settori nei quali il titanio e le sue leghe sono poco conosciuti.
Noi stiamo da tempo dedicando risorse e attività alla diffusione del titanio nell'industria ed è di grande incoraggiamento il vedere oggi così numerosi convenuti. Vi preghiamo di fare domande perché questa è l'occasione specificamente dedicata alla vostra partecipazione attiva, ed è proprio la finalità di questo convegno l'informare.

Un altro obiettivo che ci proponiamo è il miglioramento della immagine del titanio; come sapete ancora oggi in molti settori dell'industria il titanio è ancora considerato materiale sofisticato, strategico, militare, costoso…, invece non è vero: in questi anni il titanio sta dimostrandosi nella sua vera vocazione di metallo strutturale, alta resistenza alla corrosione, con un peso intermedio fra acciai e alluminio, adatto a tantissime applicazioni terrestri e industriali che vanno dai mezzi di trasporto alle grandi opere civili e autostradali, dall’industria alimentare agli impianti ecologici, dalla cantieristica agli impianti offshore petroliferi… ad altre nuove applicazioni di cui sentiremo parlare dai nostri oratori, ai quali non voglio sottrarre tempo.

Desidero però ricordare alcuni avvenimenti importanti nel settore del titanio in Italia degli scorsi 12 mesi.

Come vedete anche dagli stendardi ho il piacere di annunciare che è nata la nostra nuova società Ginatta Torno Titanium (GTT), che è stata formata con la società Torno di Milano e costituisce il potenziamento della nostra Divisione Titanio precedente, per essere sempre più efficace nella commercializzazione di impianti per la produzione del titanio in tutto il mondo.

A questo proposito la costruzione dell’impianto USA è quasi ultimata e a dicembre inizieremo i collaudi.

Per quanto riguarda l’impianto in Italia stiamo mettendo a punto gli ultimi dettagli con la società Titania di Terni e siamo fiduciosi di iniziare la costruzione la prossima primavera insieme con la società Italimpianti.

Abbiamo voluto citare queste notizie non per dirette finalità commerciali, ma come elementi per stimolare le decisioni di utilizzare il titanio; infatti la disponibilità a magazzino dei semilavorati sarà sempre più garantita dall’entrata in funzione degli impianti citati e di conseguenza la stabilità dei prezzi potrà essere raggiunta per lo sviluppo vigoroso del mercato del titanio.

Adesso (novità rispetto agli altri anni) abbiamo il grandissimo piacere, ed io sono personalmente commosso, nel consegnare la Targa del nostro primo premio alla persona che si è particolarmente distinta nel settore del titanio per il suo contributo alla nostra industria dagli albori negli anni '50 fino ad oggi.

Questa persona è il Sig. John Priscu.

Se posso fare una citazione personale, di oltre 20 anni fa, di quando ero studente in America, mi piace ricordare le fertili discussioni fatte da John durante il lavoro per la mia tesi sulla elettrolisi del titanio.
John infatti ha sempre lavorato nell'industria americana del titanio sia nel settore della ricerca e sviluppo dei processi, che nella organizzazione e avviamento degli impianti produttivi vissuto come Ingegnere con l'occhio al conto economico.
L'industria del titanio ricorda John per il suo lavoro pionieristico del titanio elettrolitico.

Adesso il modo migliore di iniziare i lavori del nostro convegno è proprio quello di sentire da John una testimonianza della Sua esperienza e i Suoi consigli che ci guidano nel lavoro di diffusione dell'uso del titanio nell'industria.

John E. Kosin
RMI Company - U.S.A.

TREND IN PROCESSING, FABRICATION AND APPLICATION OF TITANIUM

1 - INTRODUCTION

Prior to discussion of the text of my presentation this morning, I would like to review the availability and properties of titanium (Fig. 1).

Titanium is not a rare element. In fact, you can see (Fig. 2) that titanium is the fourth most abundant metal in the earth's crust, following after aluminium, iron and magnesium.

Titanium is well dispersed throughout the earth and, as you can see in Fig. 3, there are workable deposits of titanium ore throughout the globe. Thus, it is not sensitive to geographical or political problems that may exist in the world.

Fig. 4 shows the growth of the titanium industry by markets in the United States from 1966 through 1985.

The free world consumption of titanium would be about twice the numbers you see here. As you see, the defence usage has been fairly constant over the period. Significant growth has occurred in the commercial aerospace and industrial markets since about 1976.

From Fig. 5 you can also see that the projected free world capacity exceeds the demand. This is further illustrated (Fig. 6) when one considers that only 5% of the TiO_2 consumption goes into metal production.

So we might ask, if titanium is so abundant, if it is so well dispersed, why is it not used more?

The growth of titanium has been restricted to a certain extent by the cost of the metal, cost of winning it from the ore. It is fairly expensive in terms of energy. However, there has been a gradual decrease in the amount of energy.
There has also been a rather large increase in the usage of titanium.

So it seem reasonable to expect that the driving force for changing trends in material use is to design around the key properties of titanium, improve the performance and operating costs, while at the same time, reducing the manufacturing costs.

The key properties (Fig. 7) of titanium are fairly well known. To review, they centre around two characteristics. First of all, corrosion resistance. Titanium has excellent corrosion resistance in all natural media, including chlorides and organics, very resistant to salt water and chloride solutions.

The second main characteristic is that it has a low density, about one-half that of iron and slightly higher than aluminium.

However the metal, as you can see, has high strength capabilities. So, when you combine the low density with high strength, you have a very efficient engineering material.

Another favourable characteristic of titanium includes its high temperature strength.

Other interesting properties that, on occasion, are very useful in design applications include:

- it has very good ballistic resistance;
- it has low thermal expansion, which is very similar to that of glass and composites, so it is very compatible with those materials;
- it has a low elastic modulus, which makes it a unique spring material, a very efficient spring material;
- it has, on the corrosion side, good heat transfer;
- it is very effective in heat exchangers.

Titanium also has some very unique electrochemical characteristics, and it also has a very short radioactive half-life, which can be useful in processing uranium and spent uranium. I will expand on some examples of these properties later in my presentation.

With this in mind, I would like to review the trends in processing, fabrication and applications. Since time does not permit me to cover all aspects, I will elaborate only on those areas of major activity in the USA during the past three years.

2 - PROCESSING TRENDS

Responding to the aerospace, chemical process and electronic industries needs for high-cleanliness, high purity titanium, nonconsumable, cold-hearth melting is receiving a lot of attention. The key is cold-hearth as opposed to drip-melting directly into a cold-wall mold.

Production of these high performance engineering materials requires highly controlled processing conditions. Both demands of high purity processing environment and high performance heating source can be met using:

- Electron Beam
- Plasma

melting conditions. These technologies are similar with regard to hearth melting.

Electron-beam melting (Fig. 8) is a vacuum process which utilizes the thermal energy of the electron beam for melting and refining operations. The heat in the prevailing vacuum environment permits distillation of volatile elements including vaporization of suboxides, evolution and removal of gases, and vaporization of metal impurities with vapour pressures above that of the titanium. Most notable in titanium is aluminium, since it is common to most alloy systems.

Alec Mitchell of the University of British Columbia is working on inline compositional analyses aimed at making compositional adjustments during the melting process. Using the principles of energy dispersion analysis (EDS), Mitchell has done pioneering work in this area. The x-rays that generate the information are excited by the very energetic beam which is used to heat the surface of the liquid metal. Fig. 9 is an installation and Fig. 10 is the molten pool and metal cascading over the hearth into the mold.

Plasma-melting can be performed with a cold-hearth as well, but in an inert gas atmosphere in the pressure range of 150 mbar and 2 bar. Hence, one does not get the ultimate refinement as with a vacuum system.

Electron-beam melting is the only process which simultaneously can take advantage of the cold-hearth effect and the refining effect of high and ultra-high vacuum.

Almost since its commercial inception, prompted by the development of the gas turbine in the mid-forties, titanium has been plagued by a defect (Fig. 11) known as:

Type 1
LDI - low density inclusion
Hard Alpha
IRI - Interstitially Rich Inclusion

This defect is characterized by high hardness and higher melting point, its composition is higher in nitrogen, may also be higher in oxygen, and is usually depleted in major alloying elements. Although it is denser (approximately 15%) than molten titanium, it derives its low density connotation from the fact that it is usually associated with a void. It acts as a crack initiator and results in a premature fatigue failure.

Although an additional CEVAM has greatly reduced the incidence, inspection techniques, namely ultrasonic, which has also improved in the level of detection over the period, still remains as the last chance of preventing a defect from getting into the field.

Hence, the interest in hearth-melting, since defects that are denser than the molten metal will sink to the bottom and become entrapped in the skull which lines the hearth.

The procedure for removal of these denser materials has been coined Defect-Free Titanium (DFT).

Commercially, hearth-melting is very attractive for consolidation of scrap that otherwise would not be suitable by CEVAM. In particular, small pieces and machining chips that are generated with carbide tooling.

CEVAM (Fig. 12 and Fig. 13) begins with the fabrication of electrodes (Fig. 14) made up of compressed sponge compacts containing the alloy additions. Chemically compatible scrap can become part of the electrode makeup, but they are rather large in size because they must be individually affixed to the electrode. Smaller pieces can be included in the compact, but such additions are limited by the compact strength. One can also add limited quantities during the melting process by means of a side-feeder.

With this type of scrap processed through a cold-hearth, any segment of the electrode cross-section can be cast as dictated by the mold-configuration. Hence, the attractiveness of a combined nonconsumable hearth and CEVAM ingot.

This is reflected in the increased titanium scrap consumption in ingot (Fig. 15) for the period 82-86.

Thus, one can take advantage of the refinement afforded through cold-hearth melting and satisfy most industry specifications with subsequent CEVAM melts since alloys shall be multiple melted under vacuum or inert gas with the last melting cycle under vacuum.

3 - FABRICATION TRENDS

In fabrication, I would like to discuss two areas, namely:

- Forging;
- Superplastic Forming and/or Diffusion Bonding.

Forging

I will discuss forging from two perspectives: 1) from what is happening in the USA; 2) this combined with forging of titanium.

Thus, all my remarks relate to trends in the USA forging industry as related to only titanium forgings. First I will discuss the most popular titanium alloys used by the U.S. forging industry; this will be followed by a brief description of several developmental alloys. Second, I will discuss developmental forging techniques related to attaining net shape and improved properties. Illustrations n. 16 and 17 contain information of general interest to forgers on current popular titanium alloys. Included is the transformation temperature, the forging range, the pressures required and the general cracking resistance.

The alloys are classified in three primary groups: the alpha, the alpha-beta and the new beta. As the beta increases the cracking resistance improves, the transformation temperature decreases, the forging temperature decreases, and the pressure required decreases. As a result I suppose it is not surprising that several near beta alloys have been used or considered for forging applications. These include: 10V 2Fe 3Al (10-2-3) transage alloys and the 38-6-44 or BetaC alloy. The importance of this newer materials will be evident shortly when we discuss the advances in the forging techniques (Fig. 18). Most of the conventional forging methods can be applied to titanium and the titanium alloys: forging, hammer forging, ring rolling, mechanical or screw press forging. Because of the influence of the die chilling on the deformation characteristics, properties, structure and surface cracking, the conventional forging process does have significant liabilities. This has led to appreciable interest in technologies utilizing hot dies which have an added benefit of achieving near or net shapes.

Let us now review two key differences in conventional, on the left, versus net shape forging, on the right. These are:

- Structure/Property
- Product Yield/Cost

Fig. 19 shows studies by Dr. Chen and compares the macrostructures of Ti-6242Si alloy pancake made by the different processes. As you can readily see, the macrostructure becomes increasingly uniform as we progress from conventional to warm die to isothermal forging.

Most commercial titanium alloys are forged near 1750° F (954° C). As a result, isothermal forging - meaning die temperatures near 1750° F (954° C) is extremely difficult since:

- Die materials like IN 100 are unrepairable
- Die heating systems are complicated
- Possibility of oxygen penetration into Ti

Hot die forging is conducted using normal metal temperatures 1750° F (954° C) and die temperature near 1400° F (750° C).

Advantages are:

- wrought alloy dies Astralloy, Waspalloy: lower cost and weldable
- die heating simpler
- can produce near net and net shape

The impact of this technology is not only in improved structure control, but in achieving shapes nearer the final configuration.

Figure 20 illustrates metal utilization for various forging processes for a typical titanium alloy such as Ti-6Al-4V.

Some examples of near and net shape forgings:

Figure 21: Ti-10-2-3 Near Net Instrument Housing

Figure 22: Ti-6Al-4V Near Net Disc

Net shape (Figure 23). In this example, a transage alloy pressure vessel dome was isothermally forged at 1500° F (800° C). Top surface with bosses was forged net. Machining was required only on the top of the bosses to get the desired flatness and inside the dome which was a simple turning operation.

A cost comparison (Figure 24) of several processes by Kuhlman of Alcoa shows the advantage of net shape forgings of beta-type alloys.

This analysis was done on an engine mount and is based upon production of 100 forgings. In summary, the machined part from plate is 10% greater than a close-die part. However, the net 10-2-3 is 40% less expensive.

As you can see, new developments are being driven by reduced cost through net shape forgings or improved performance through property optimization.

4 - SUPERPLASTIC FORMING/DIFFUSION BONDING

Since superplastic forming and/or diffusion bonding offers major savings in weight and manufacturing cost, there is increased interest in the feasibility of applying the techniques to the manufacture of a range of complex structural aerospace components.

Diffusion Bonding is sometimes called diffusion welding. It is a solid state welding process in which the surfaces are placed in proximity under a moderate pressure at elevated temperature. Coalescence occurs across the interface. Because diffusion bonding requires heat, pressure and a vacuum, inert gas or a reducing atmosphere, equipment is frequently custom built by the user.

Figure 25 is a wing carry through fabricated by diffusion bonding 533 individual details.
Superplastic forming of titanium plate and sheet was also developed as a reduced-cost method for processing of material.

From Figure 26, it can be seen that most of the titanium alloys can be formed superplastically. The M-value or strain rate sensitivity factor is a measure of superplasticity of the alloy at a given strain rate. Any value greater than 0.5 is considered a candidate for superplastic forming. In conjunction with typical SPF elongation, it can be seen that Ti-6Al-4V is the most desirable candidate. In Figure 27 one can see the influence of grain size on flow stress. RMI has a grain size of 5µm. At this grain size, one can see how the flow stress and M-factor are enhanced for superplastic forming. Figure 28 is the typical microstructure of RMI sheet. Note that the microstructures are similar before and after a simulated SPF cycle.

Figure 29 is an example of the superplastic forming process. These are examples of free blowing. That is, the final geometry is not restricted or controlled by dies.

For the sphere, clean and treated sheets are edge-welded to exclude air, but a pipe is attached for pressurization. After bringing the unit to temperature, gas pressure, usually argon, is applied until the desired shape has been achieved.

A combination of superplastic forming and diffusion (SPF/DB) is being used on titanium to produce complex structures. Figure 30 is an example of the process. The sheets are prepared as with SPF, except they are treated with stop offs where bonding is not desired. Initial bonding occurs under pressure at temperature and then internal pressure, through the pipe, causes superplastic flow of the outer two sheets to fill the die and create the configuration shown.

Integrally stiffened structures are produced in this manner.

Following are examples (Figures 31, 32 and 33) of some superplastically formed parts. Note the generally smaller bend radii, deeper drawability and larger size that can be achieved as compared to standard hot-formed (Figure 34) parts.

One U.S. aerospace company is superplastically forming a part that previously consisted of seven individually hot formed parts that were joined by conventional means, one can really see the attractiveness of these fabrication methods for producing hardware.

Spurred by the aerospace industry’s use of titanium discovery of titanium’s excellent corrosion performance opened up a host of unique applications for design engineering in the early 1960’s. Titanium corrosion resistance in neutral to oxidizing environments is mainly due to a surface oxide layer. Engineers in the chemical process industries, quick to exploit this characteristic, were the first to apply titanium. At the same time titanium unique electrochemical characteristics revolutionized the chloro-alkali industry through the use of precious metal coated titanium anodes. From these first two industrial markets, titanium has expanded its non-aerospace presence into more than 25 distinct market segments.
Figure 35 is the distribution and growth of those markets.

Its weaknesses include poor corrosion resistance to reducing acids, red fuming, nitric acids and hot organic acids. If we look at the general properties of titanium there are a few observations that need to be made (Fig. 36). As one moves towards the alpha alloys there is improved corrosion to oxidizing environments at low to moderate strength levels. As one moves to the beta alloys there is improved corrosion resistance to reducing environments at higher strength levels.

Alloyed versions including small amounts of palladium and molybdenum increase the titanium resistance to reducing acids. Additions of aluminum and vanadium increase the strength and slightly reduce the range in the oxidizing region. But note the beta alloy, the Beta C (Fig. 37), with the high attainable strength up to 315° C and the range in both the oxidizing and reducing sides. In the search for alternate energy sources, it is not surprising that this alloy is rapidly gaining acceptance in geothermal and sour gas wells.

5 - GEOTHERMAL

In geothermal, energy is extracted from the earth in the form of high temperature hypersaline brines. Some of these brines also contain H_2S and CO_2 at temperature ranges of 450° - 600° F (232° - 315° C). These brines impose severe restrictions on metals with limited corrosion resistance. In addition, high strength and heat treatability are required due to the large piping employed. In fact, beta titanium may be the only economical way to produce energy using geothermal technology. Figure 38 is an example of geothermal applications.

6 - SOUR GAS

Fossil fuel shortages have forced the oil and gas industries to produce more corrosive deposits. These deposits typically contain hydrogen sulphide (hence the term “sour”), pose an exceptional challenge to the materials engineer.

Figure 39 shows the Beta C^{TM} advantages in the oil field market. These include high strength, corrosion resistance and low density, which are all necessary for successful usage. In addition, the low elastic modulus makes it nearly perfect for

Figure 40, one can see the uses of Beta C^{TM} for down-hole applications.

Figure 41 and 42 are some of the casings and strings being used in these installations. From their size and quantity, it is easy to see the tremendous usage potential in these markets.

In summary, titanium usage will continue to grow based upon its unique combination of properties aided by improved performance and reduced total cost of the entire system.


STRENGTH
DURABILITY
LIGHT WEIGHT
CORROSION RESISTANCE
TITANIUM

Fig. 1 - Titanium properties

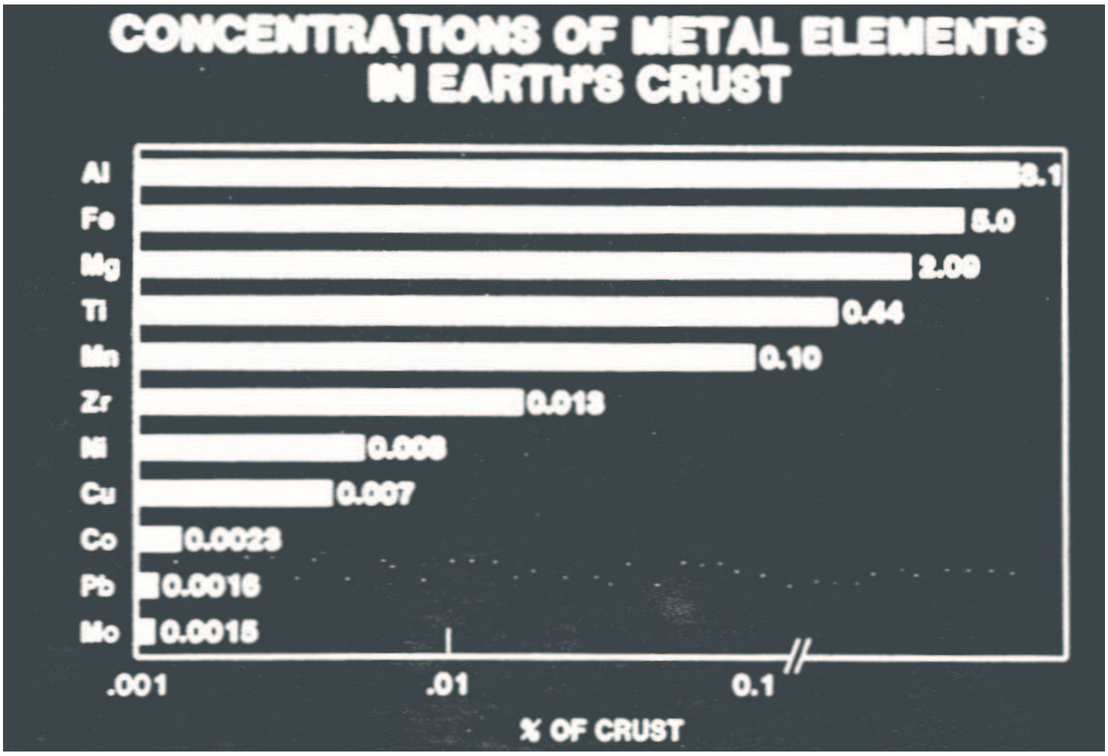


Fig. 2 - Relative abundance of materials in the heth's crust

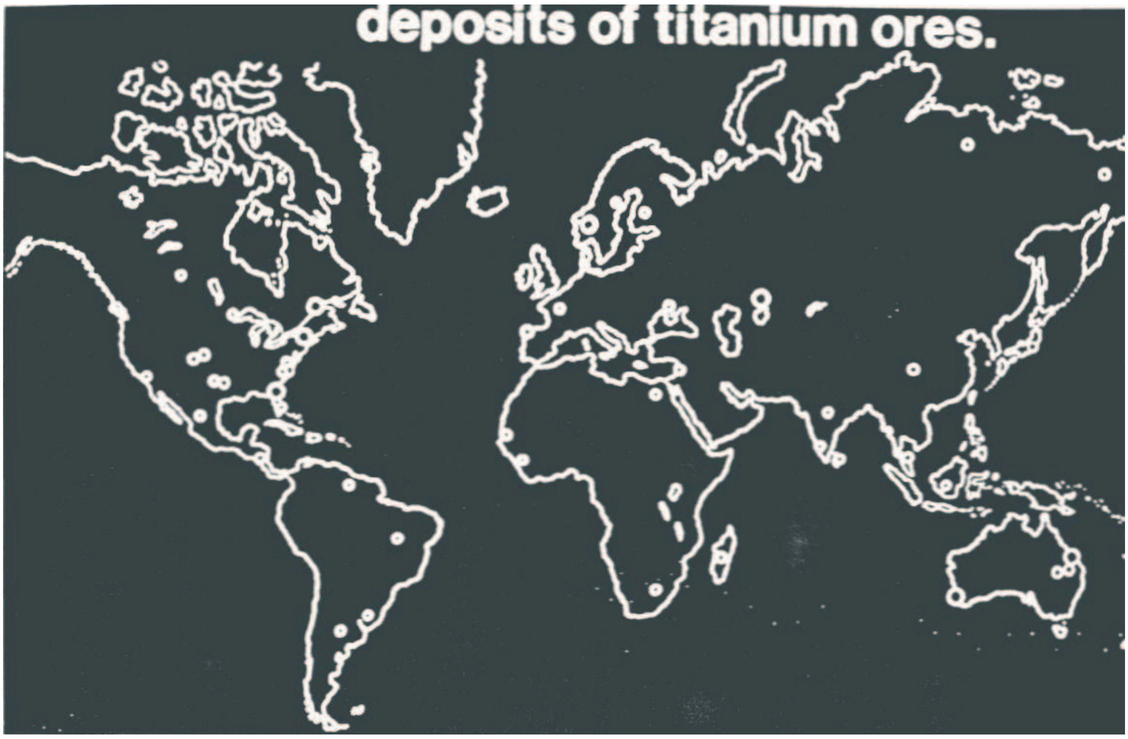


Fig. 3 - Deposits of Titanium ores throughout the globe

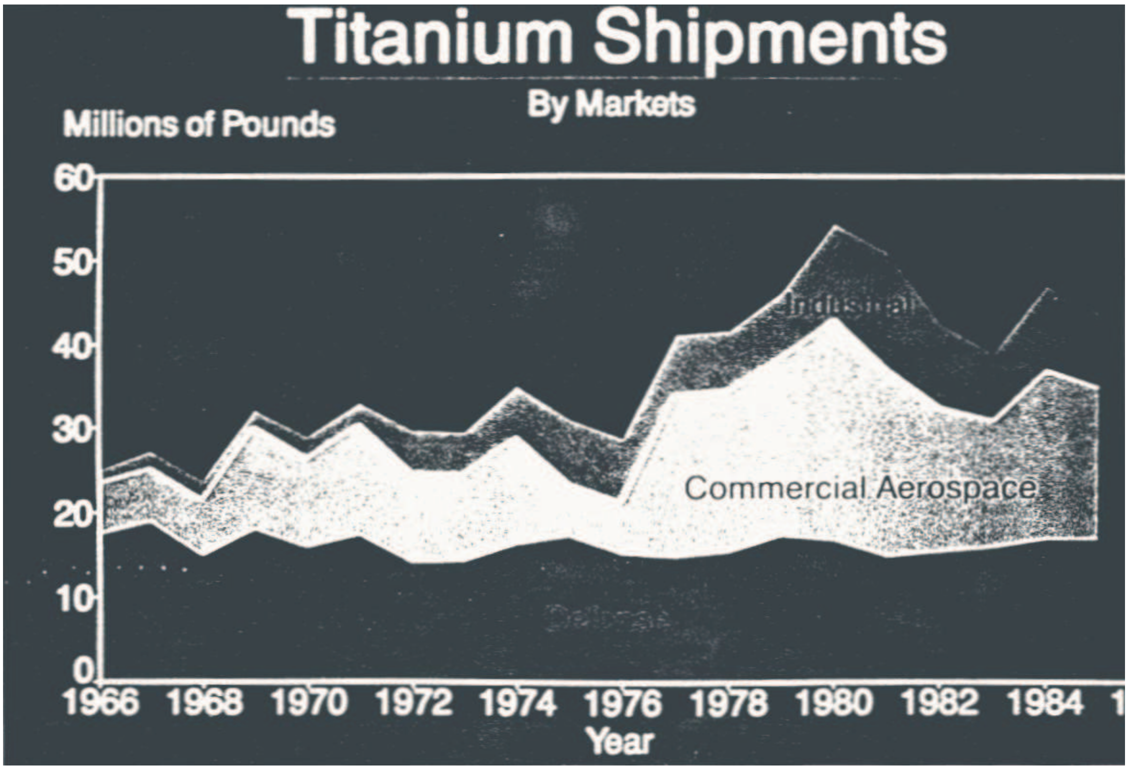


Fig. 4 - Growth of the titanium industry by markets in the U.S. from 1966 through 1985

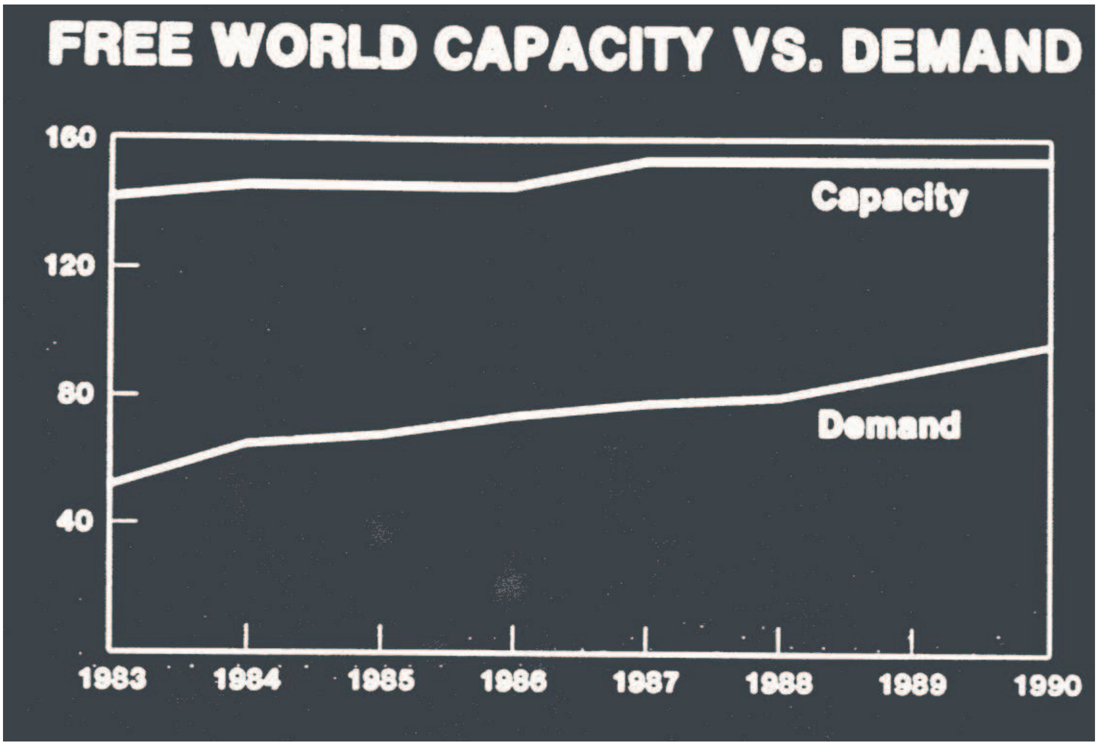


Fig. 5 - Projected free world capacity and demand

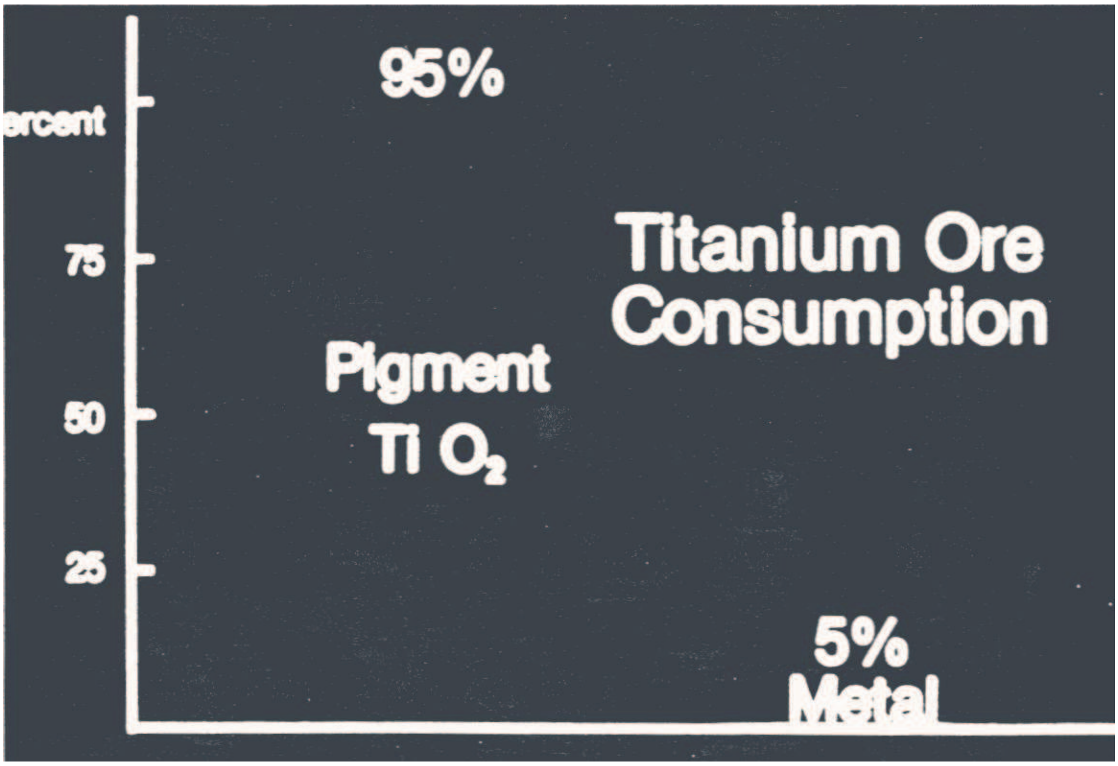


Fig. 6 - Titanium ore consumption

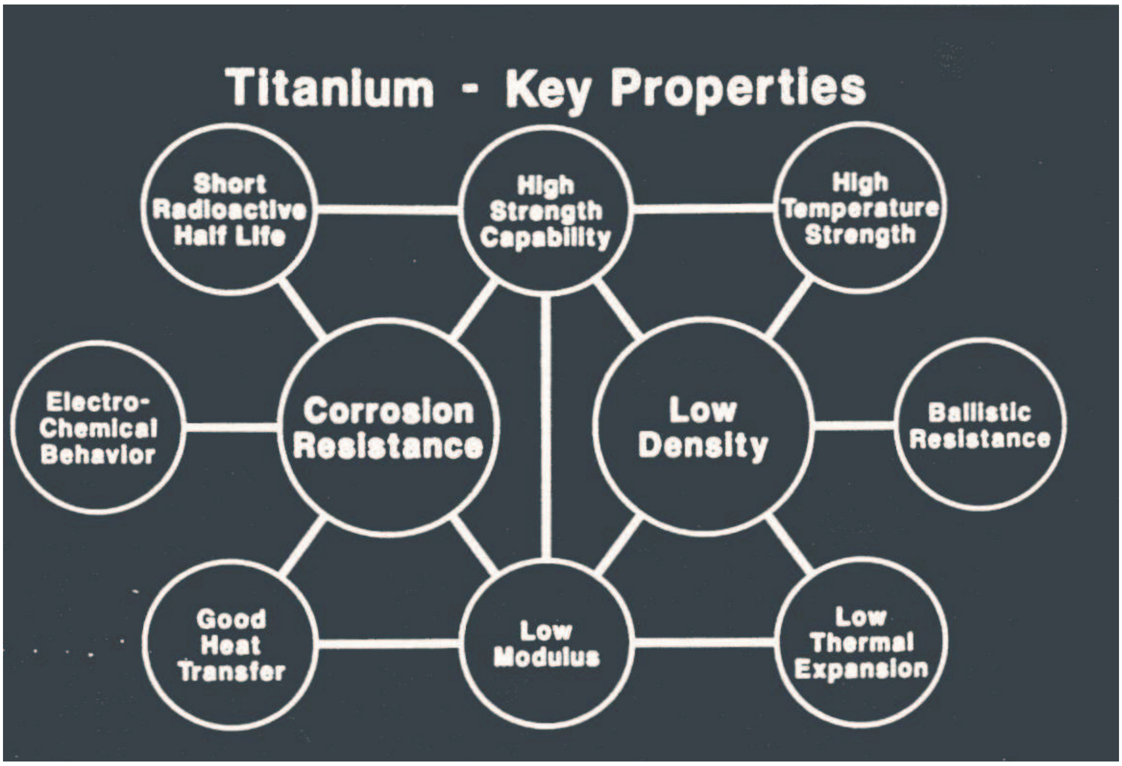


Fig. 7 - Titanium key properties

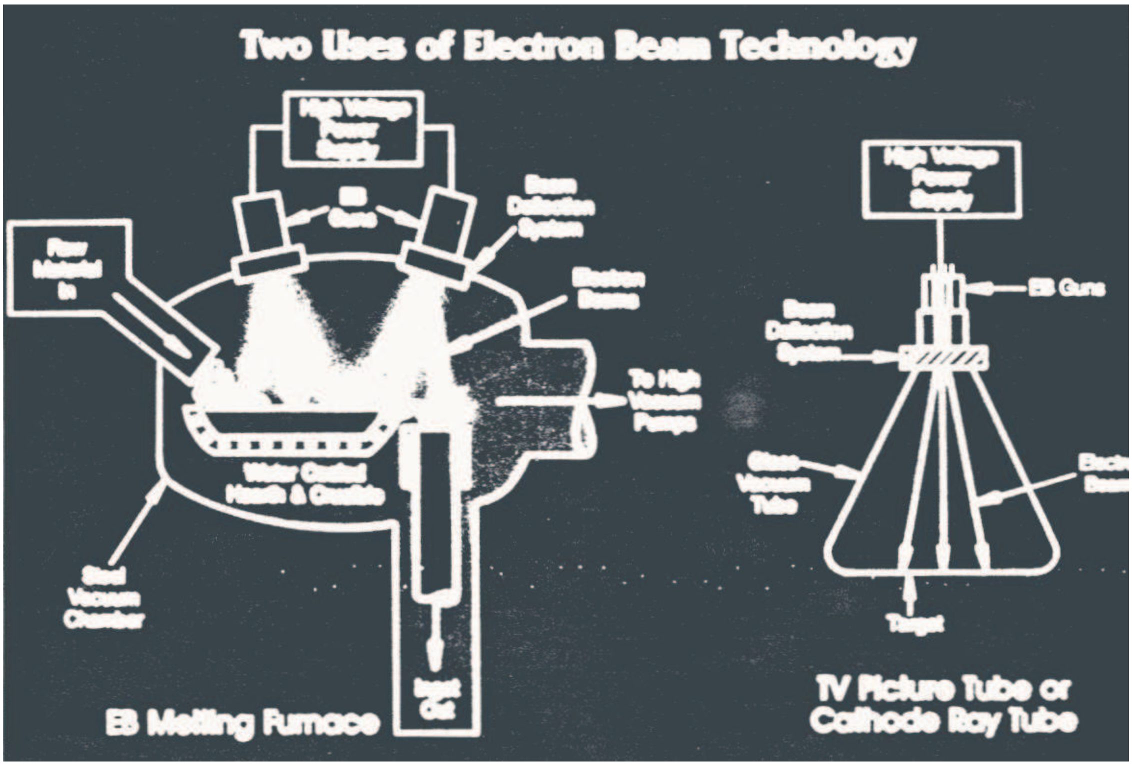


Fig. 8 - Electron beam processes

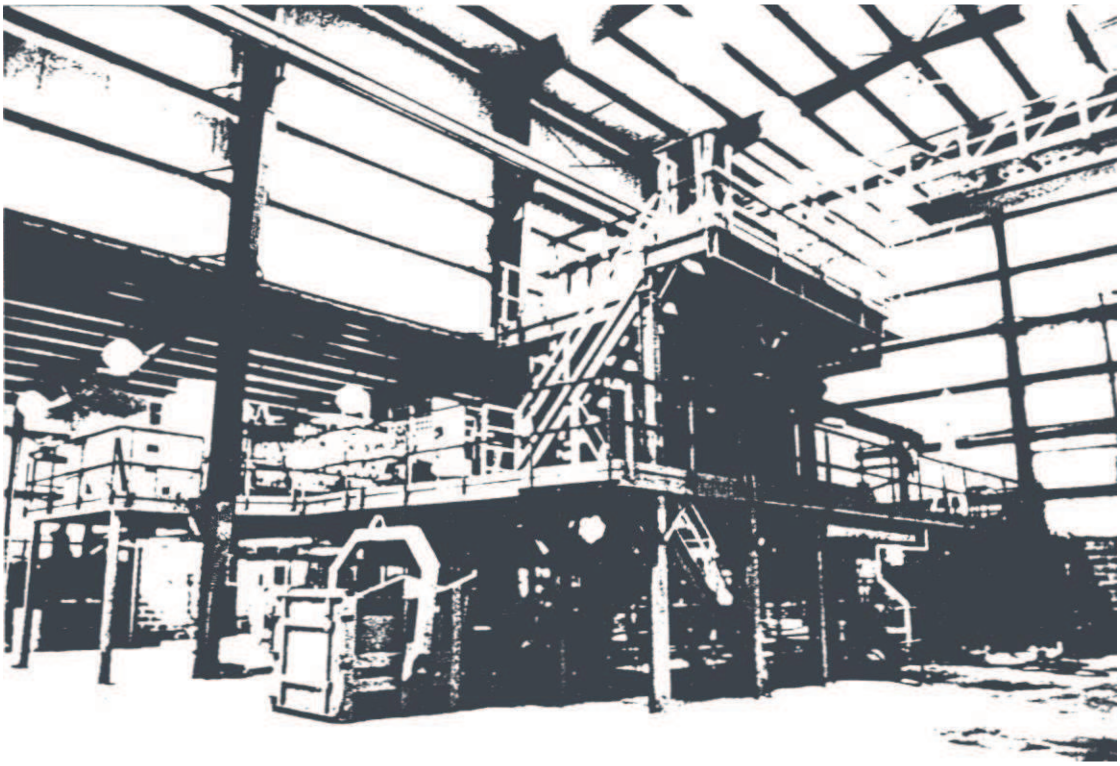
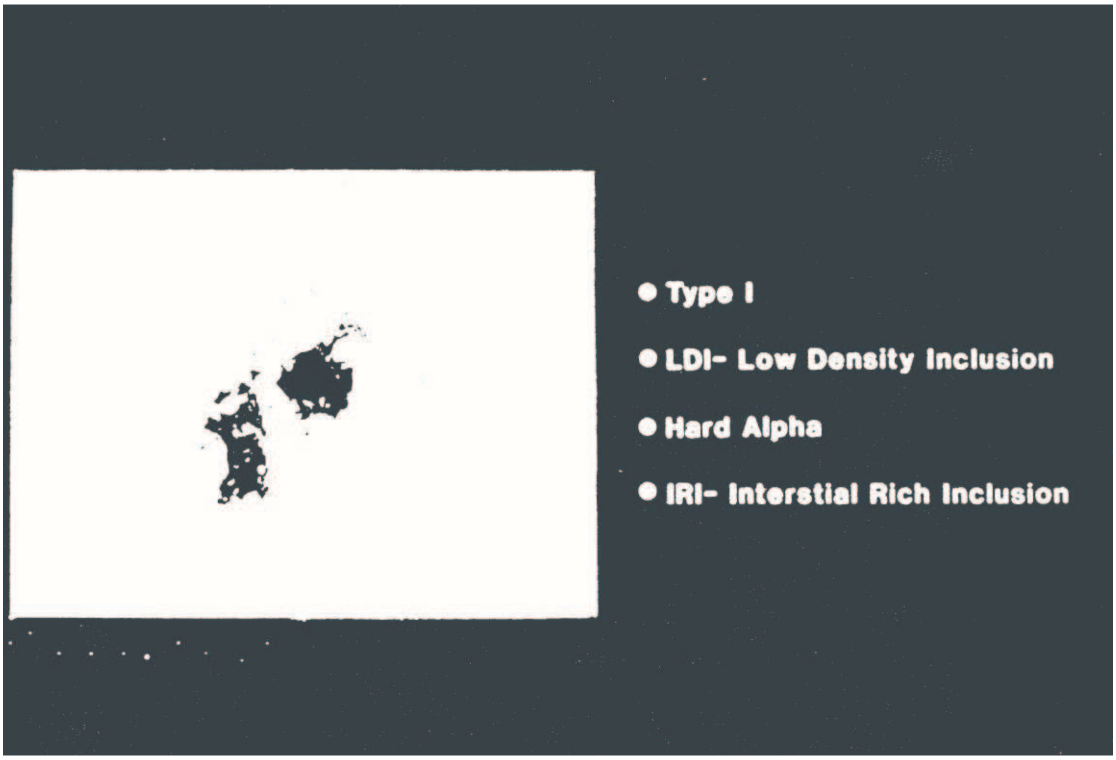


Fig. 9 - Electron beam installation

Fig. 10 - Molten metal flow in the electron beam cold earth



- Type I
- LDI- Low Density Inclusion
- Hard Alpha
- IRI- Interstial Rich Inclusion

Fig. 11 - Type I defect in titanium

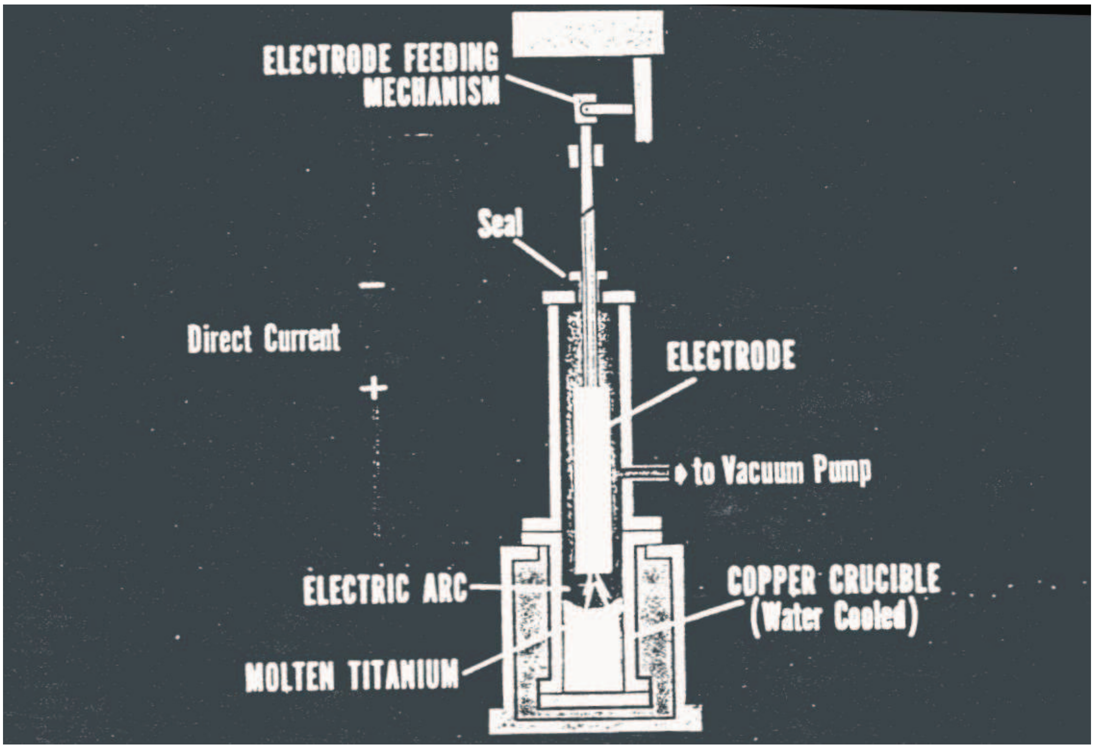


Fig. 12 - Consumable electrode vacuum arc melting (CEVAM) furnace diagram

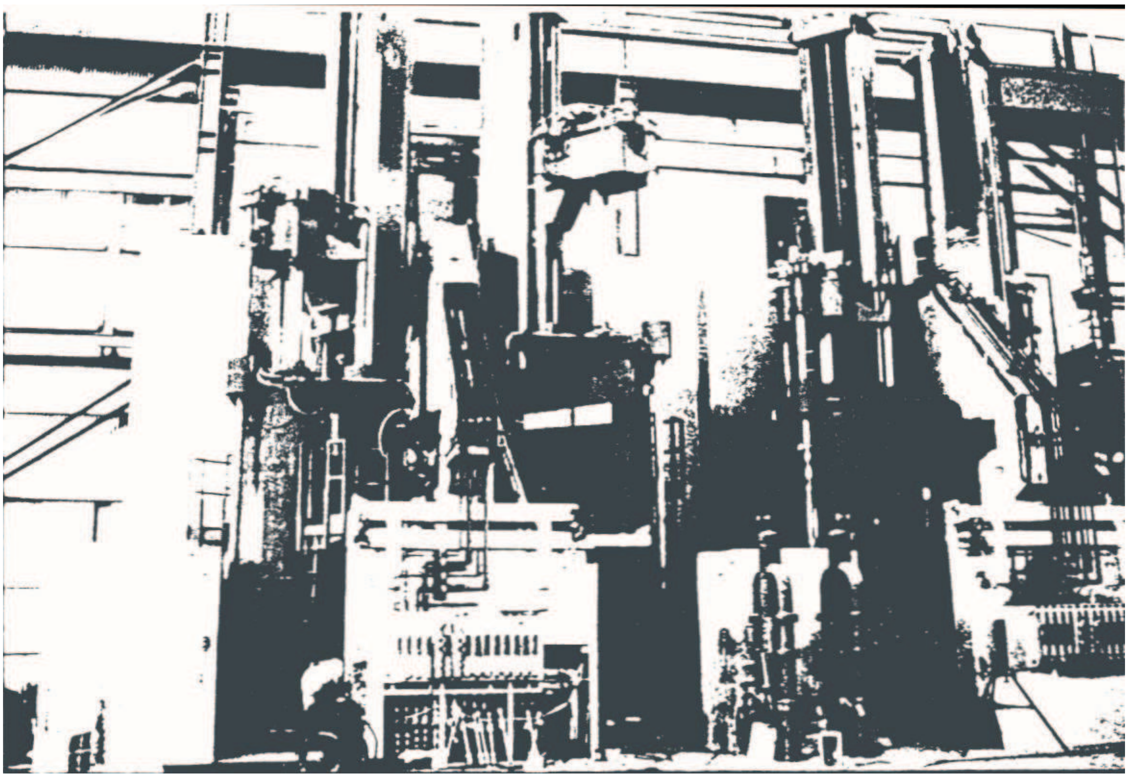


Fig. 13 - CEVAM furnace at RMI

Fig. 14 - Compressed sponge electrodes

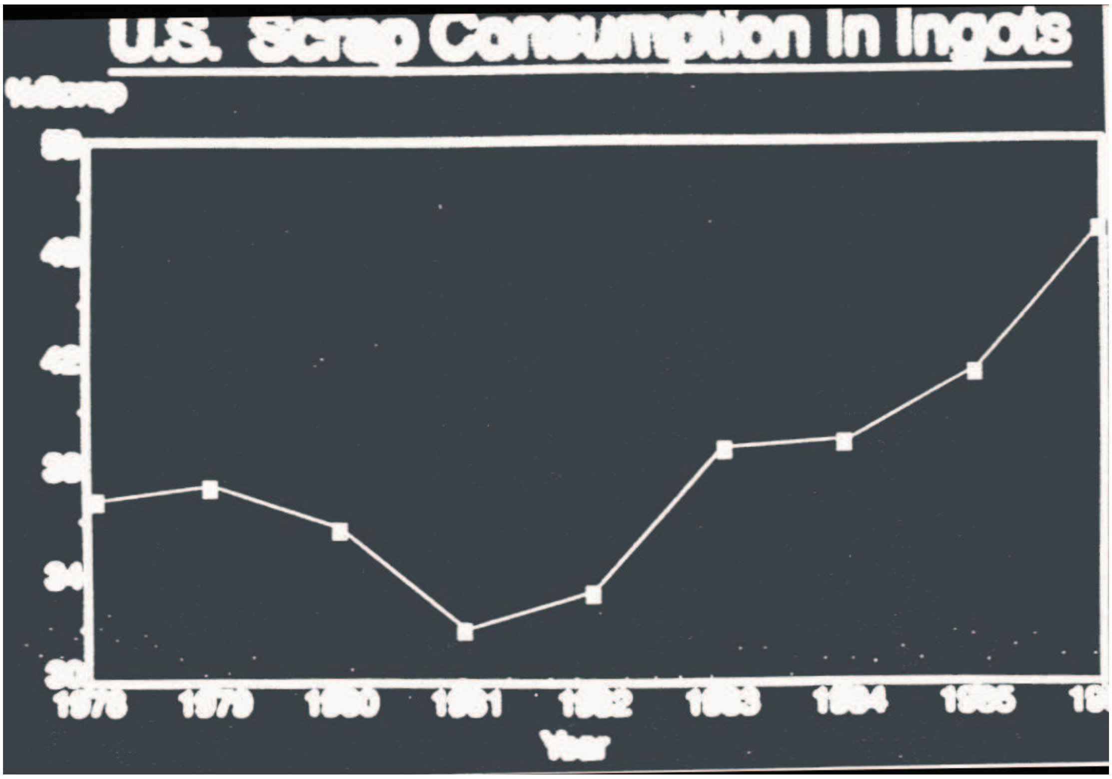
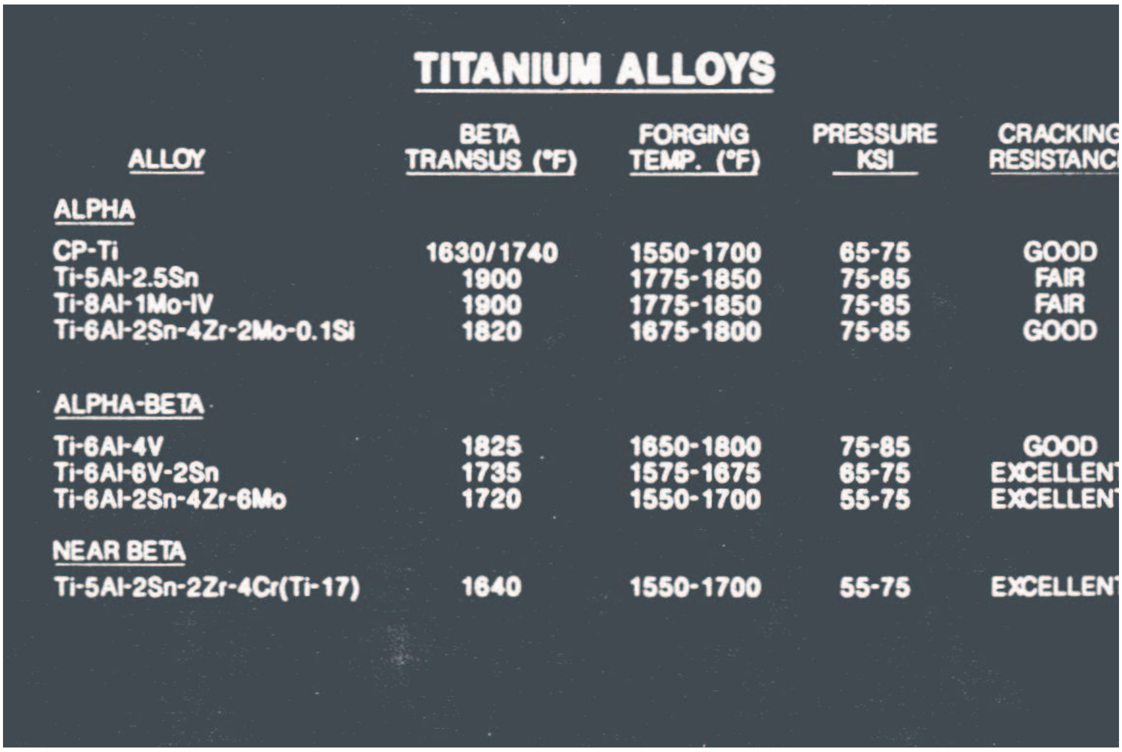


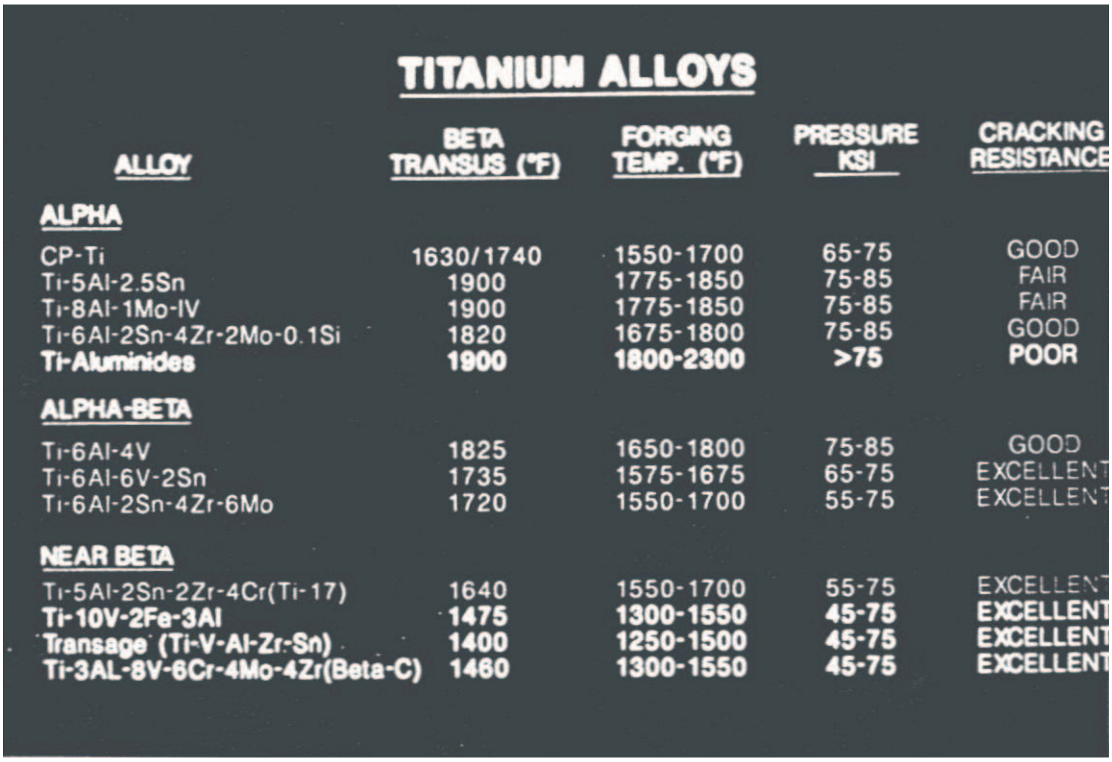
Fig. 15 - U.S. scrap consumption trend



TITANIUM ALLOYS

ALLOY	BETA TRANSUS (°F)	FORGING TEMP. (°F)	PRESSURE KSI	CRACKING RESISTANC
ALPHA				
CP-Ti	1630/1740	1550-1700	65-75	GOOD
Ti-5Al-2.5Sn	1900	1775-1850	75-85	FAIR
Ti-8Al-1Mo-IV	1900	1775-1850	75-85	FAIR
Ti-6Al-2Sn-4Zr-2Mo-0.1Si	1820	1675-1800	75-85	GOOD
ALPHA-BETA				
Ti-6Al-4V	1825	1650-1800	75-85	GOOD
Ti-6Al-6V-2Sn	1735	1575-1675	65-75	EXCELLENT
Ti-6Al-2Sn-4Zr-6Mo	1720	1550-1700	55-75	EXCELLENT
NEAR BETA				
Ti-5Al-2Sn-2Zr-4Cr(Ti-17)	1640	1550-1700	55-75	EXCELLENT

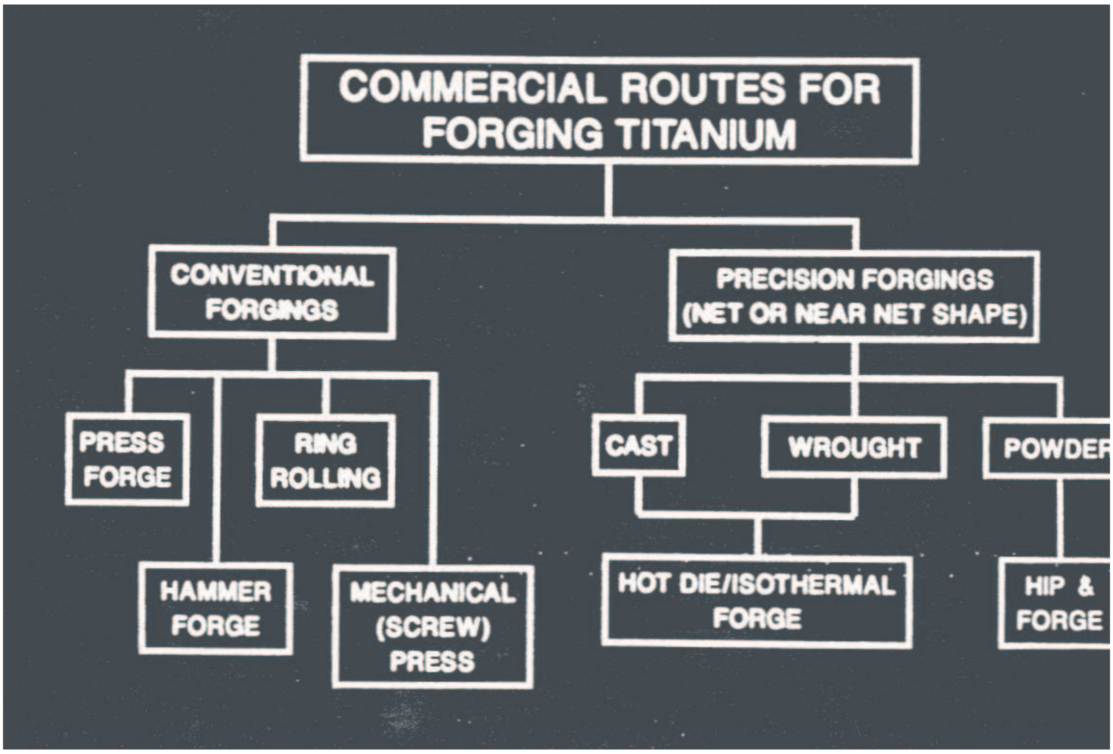
Fig. 16 - Forging for titanium alloys



TITANIUM ALLOYS

ALLOY	BETA TRANSUS (°F)	FORGING TEMP. (°F)	PRESSURE KSI	CRACKING RESISTANCE
ALPHA				
CP-Ti	1630/1740	1550-1700	65-75	GOOD
Ti-5Al-2.5Sn	1900	1775-1850	75-85	FAIR
Ti-8Al-1Mo-IV	1900	1775-1850	75-85	FAIR
Ti-6Al-2Sn-4Zr-2Mo-0.1Si	1820	1675-1800	75-85	GOOD
Ti-Aluminides	**1900**	**1800-2300**	**>75**	**POOR**
ALPHA-BETA				
Ti-6Al-4V	1825	1650-1800	75-85	GOOD
Ti-6Al-6V-2Sn	1735	1575-1675	65-75	EXCELLENT
Ti-6Al-2Sn-4Zr-6Mo	1720	1550-1700	55-75	EXCELLENT
NEAR BETA				
Ti-5Al-2Sn-2Zr-4Cr(Ti-17)	1640	1550-1700	55-75	EXCELLENT
Ti-10V-2Fe-3Al	**1475**	**1300-1550**	**45-75**	**EXCELLENT**
Transage (Ti-V-Al-Zr-Sn)	**1400**	**1250-1500**	**45-75**	**EXCELLENT**
Ti-3AL-8V-6Cr-4Mo-4Zr(Beta-C)	**1460**	**1300-1550**	**45-75**	**EXCELLENT**

Fig. 17 - Forging conditions for titanium alloys



COMMERCIAL ROUTES FOR FORGING TITANIUM

CONVENTIONAL FORGINGS

PRESS FORGE

RING ROLLING

HAMMER FORGE

MECHANICAL (SCREW) PRESS

PRECISION FORGINGS (NET OR NEAR NET SHAPE)

CAST

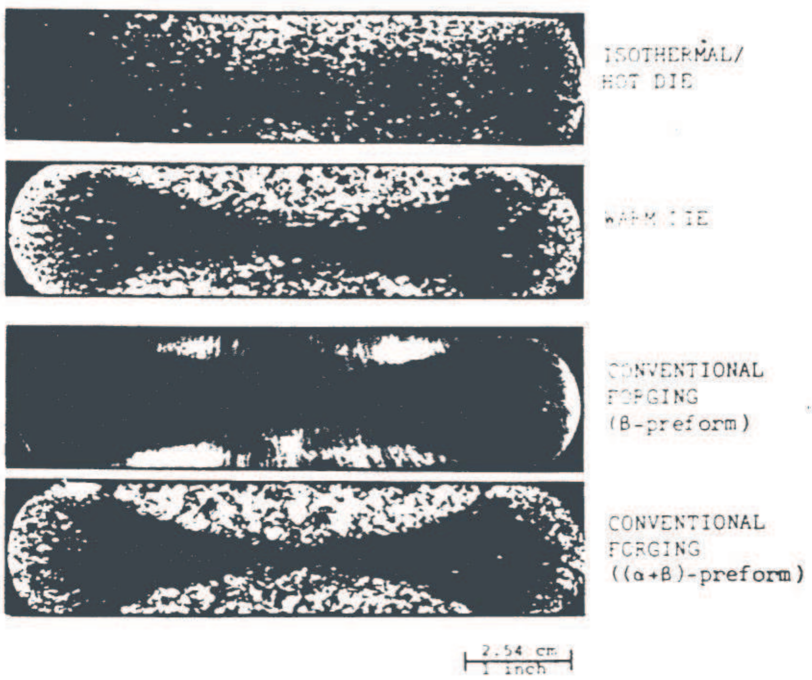
WROUGHT

POWDER

HOT DIE/ISOTHERMAL FORGE

HIP & FORGE

Fig. 18 - Commercial techniques for forging titanium



. Comparison of Macrostructures between Isothermally and Conventionally Forged Ti-6242Si Alloy Pancakes.

Fig. 19 - Macrostructure comparison in different Ti-6242Si forgings

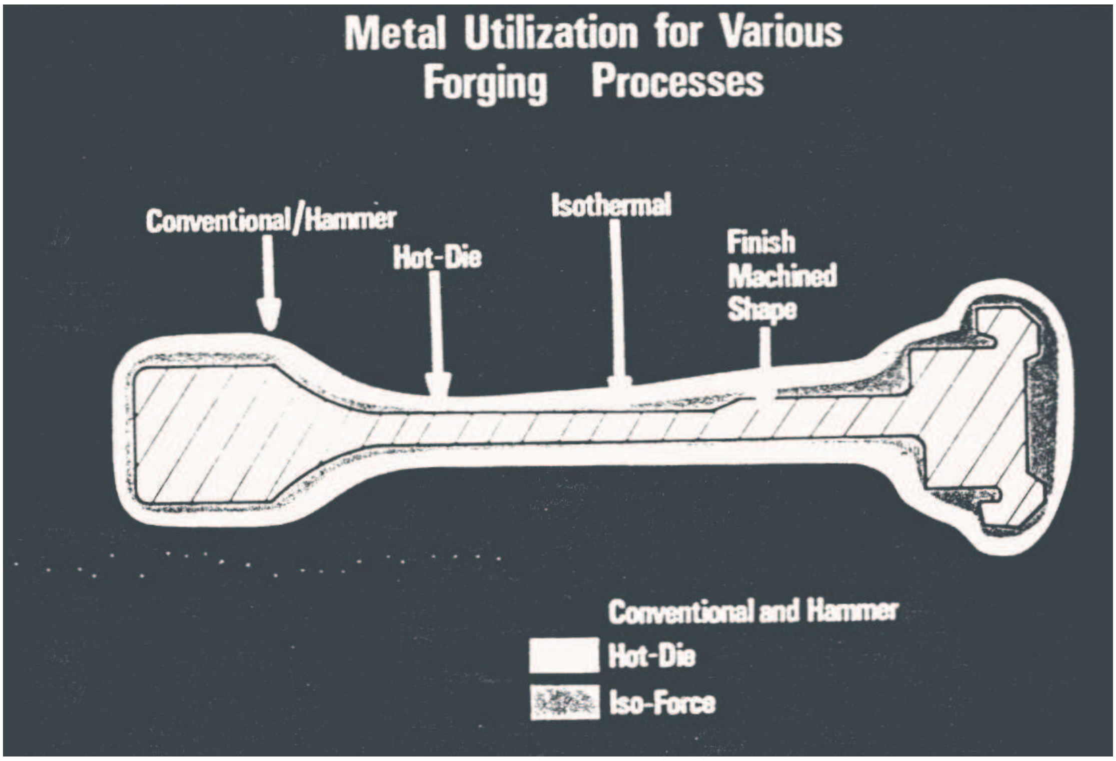


Fig. 20 - Metal utilisation for various forging processes

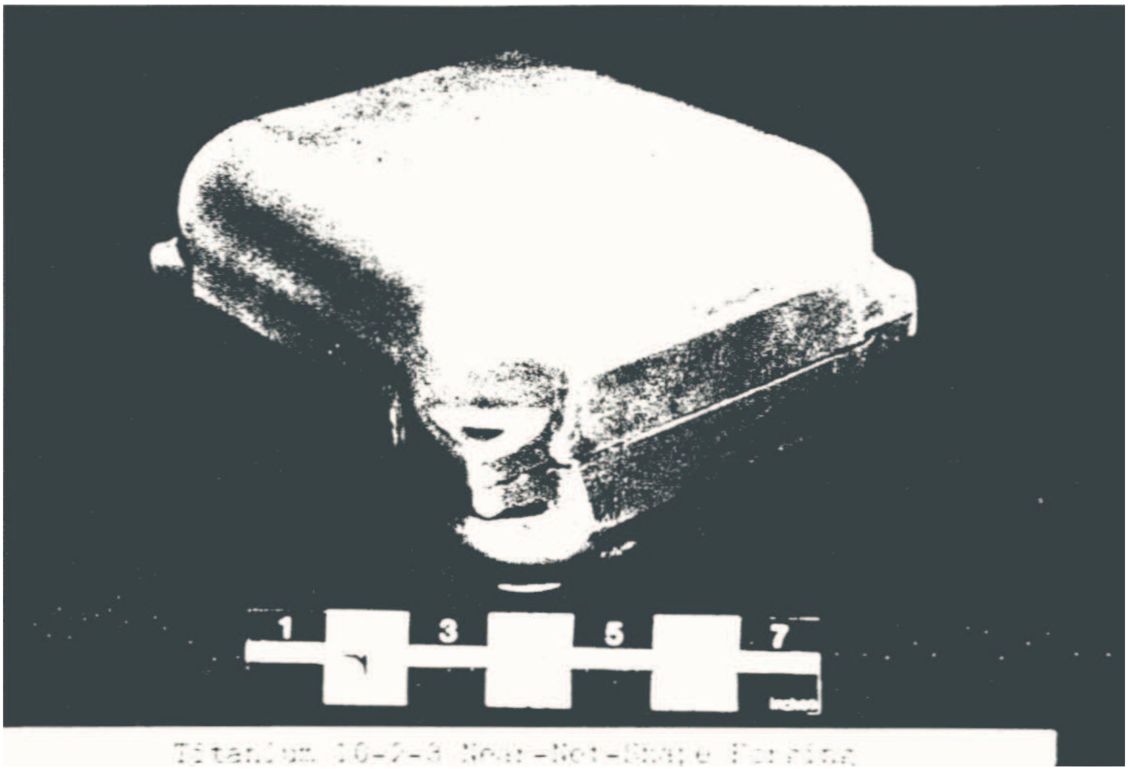
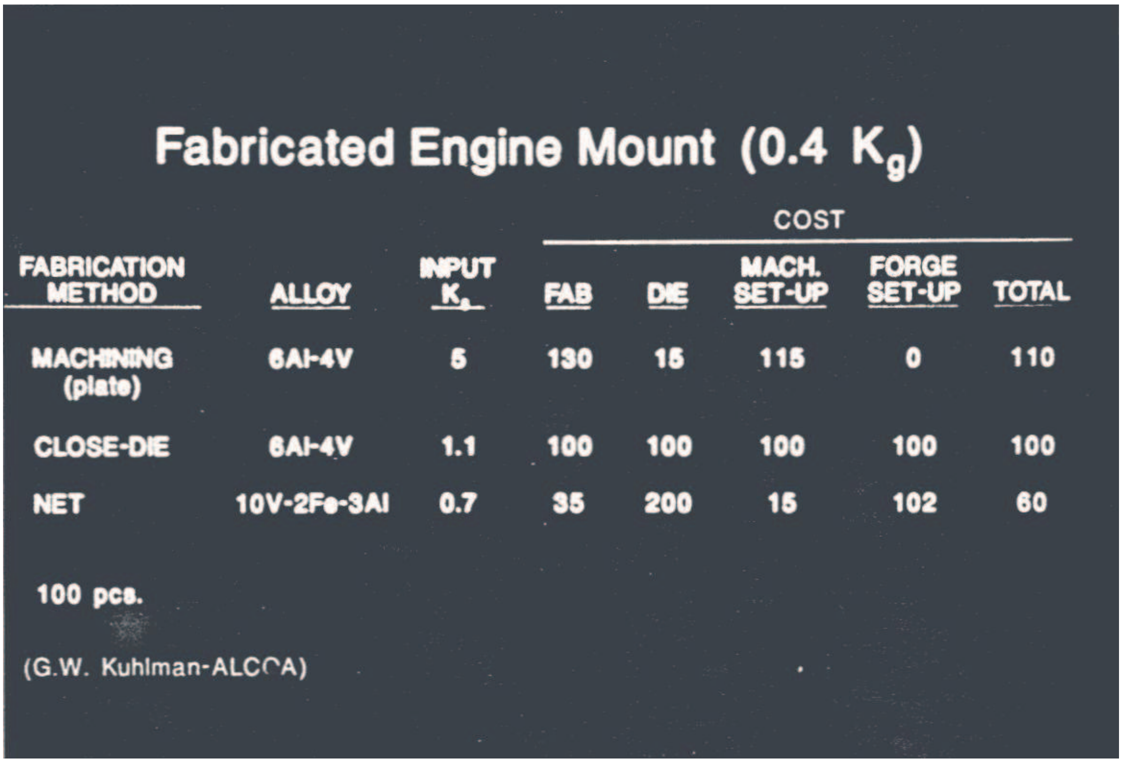


Fig. 21 - 10-2-3 near net shape instrument housing

Fig. 22 - Near net shape disc

Fig. 23 - Transage alloy isothermal forging



Fabricated Engine Mount (0.4 K_g)

FABRICATION METHOD	ALLOY	INPUT K_g	COST FAB	DIE	MACH. SET-UP	FORGE SET-UP	TOTAL
MACHINING (plate)	6Al-4V	5	130	15	115	0	110
CLOSE-DIE	6Al-4V	1.1	100	100	100	100	100
NET	10V-2Fe-3Al	0.7	35	200	15	102	60

100 pcs.

(G.W. Kuhlman-ALCOA)

Fig. 24 - Cost comparison in various fabrication methods

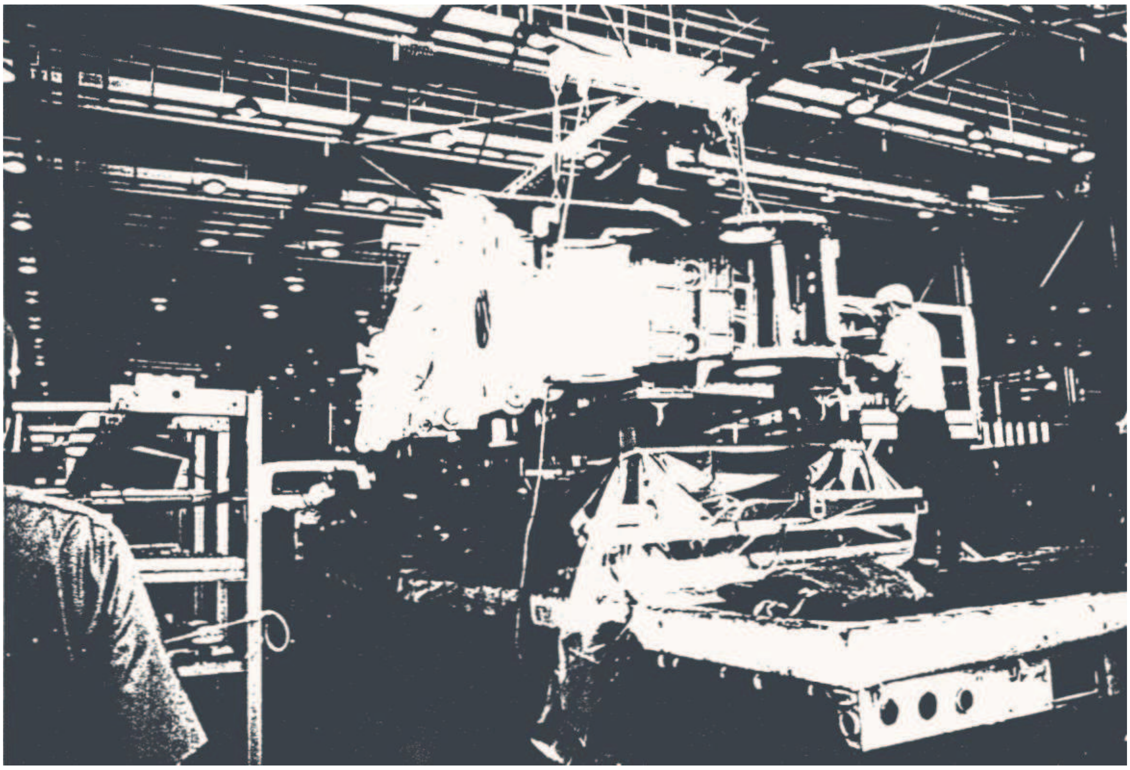
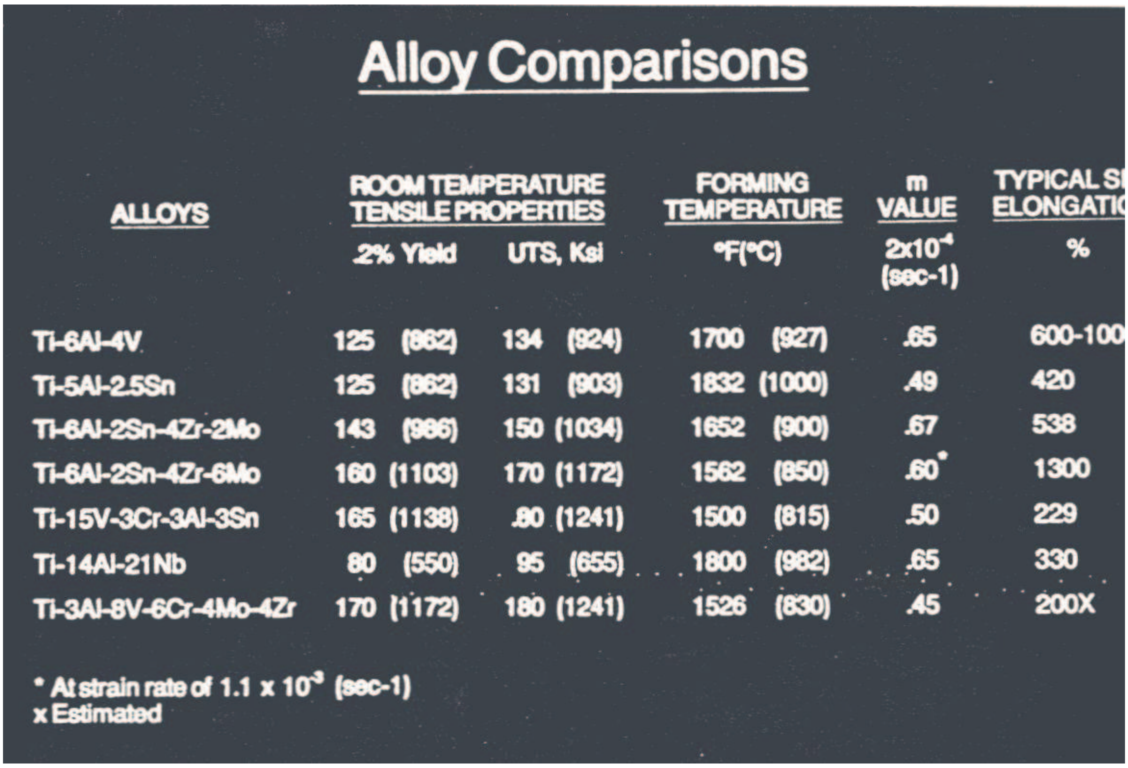


Fig. 25 - Wing carry through structure fabricated by diffusion bonding

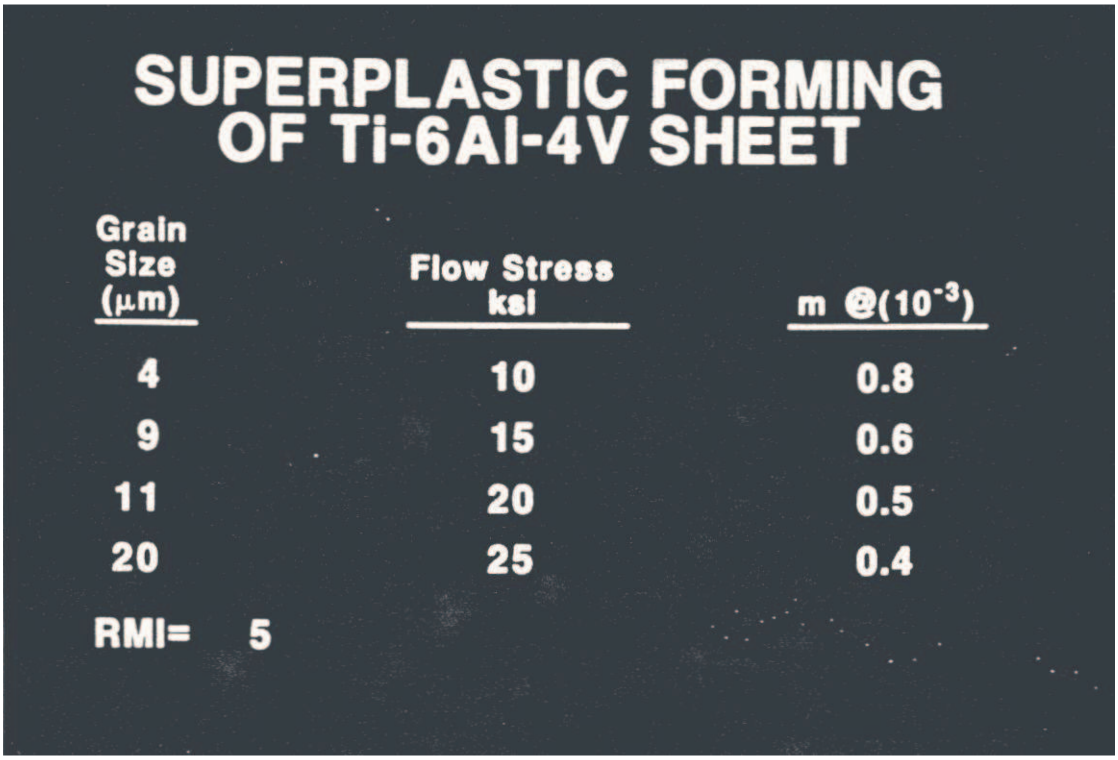


Alloy Comparisons

ALLOYS	ROOM TEMPERATURE TENSILE PROPERTIES		FORMING TEMPERATURE	m VALUE	TYPICAL S ELONGATI
	.2% Yield	UTS, Ksi	°F(°C)	$2x10^{-4}$ (sec-1)	%
Ti-6Al-4V	125 (862)	134 (924)	1700 (927)	.65	600-100
Ti-5Al-2.5Sn	125 (862)	131 (903)	1832 (1000)	.49	420
Ti-6Al-2Sn-4Zr-2Mo	143 (986)	150 (1034)	1652 (900)	.67	538
Ti-6Al-2Sn-4Zr-6Mo	160 (1103)	170 (1172)	1562 (850)	.60*	1300
Ti-15V-3Cr-3Al-3Sn	165 (1138)	.80 (1241)	1500 (815)	.50	229
Ti-14Al-21Nb	80 (550)	95 (655)	1800 (982)	.65	330
Ti-3Al-8V-6Cr-4Mo-4Zr	170 (1172)	180 (1241)	1526 (830)	.45	200X

* At strain rate of 1.1 x 10^{-3} (sec-1)
x Estimated

Fig. 26 - SPF characteristics for various Ti alloys



SUPERPLASTIC FORMING OF Ti-6Al-4V SHEET

Grain Size (μm)	Flow Stress ksi	m @(10^{-3})
4	10	0.8
9	15	0.6
11	20	0.5
20	25	0.4

RMI= 5

Fig. 27 - Influence of grain size on flow stress

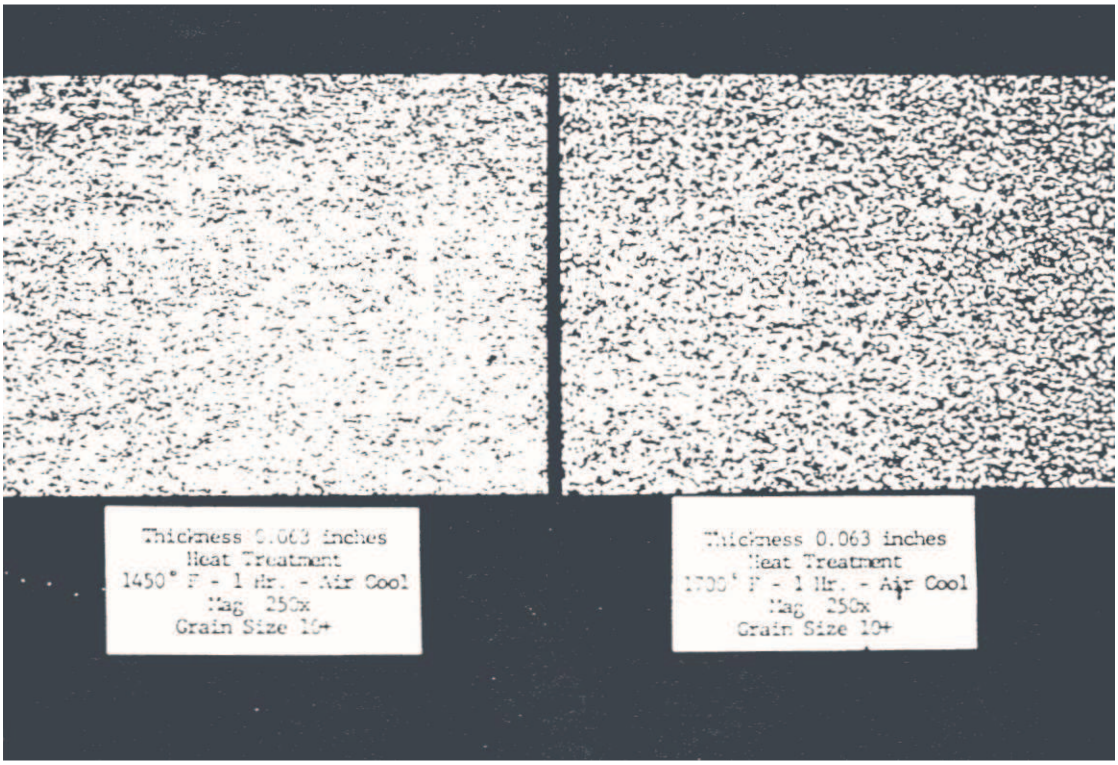


Fig. 28 - Typical microstructure of RMI sheet

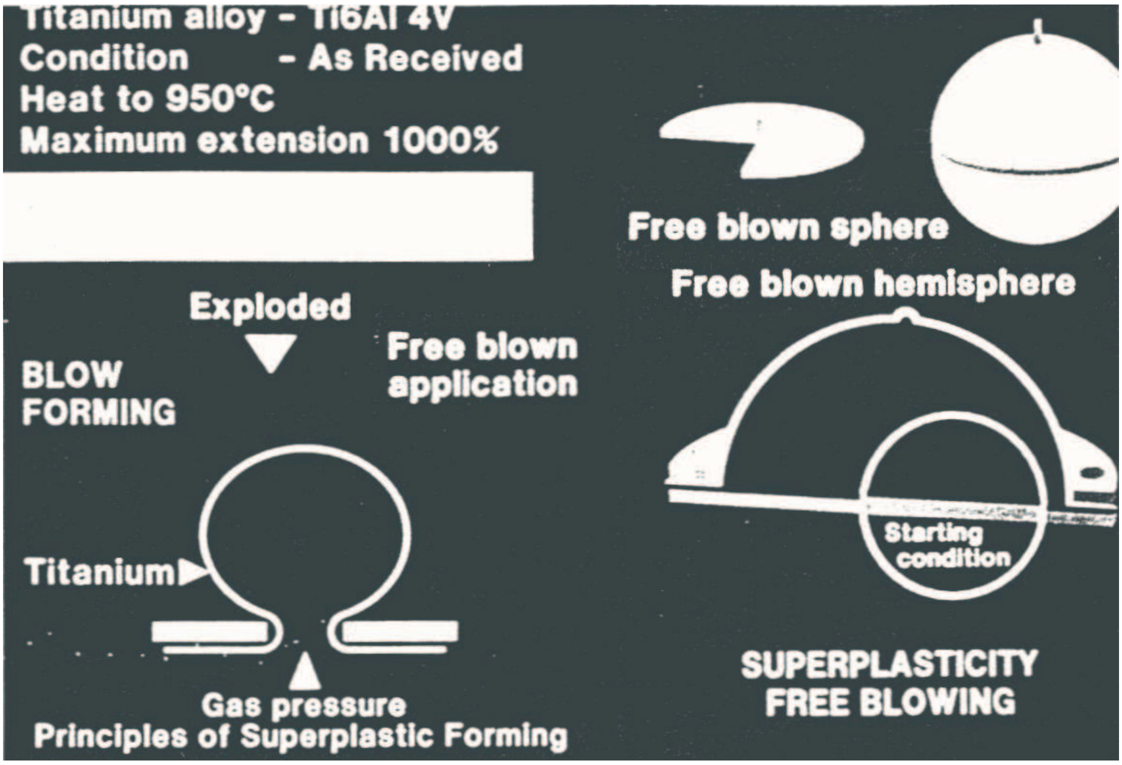


Fig. 29 - Examples of SPF processes

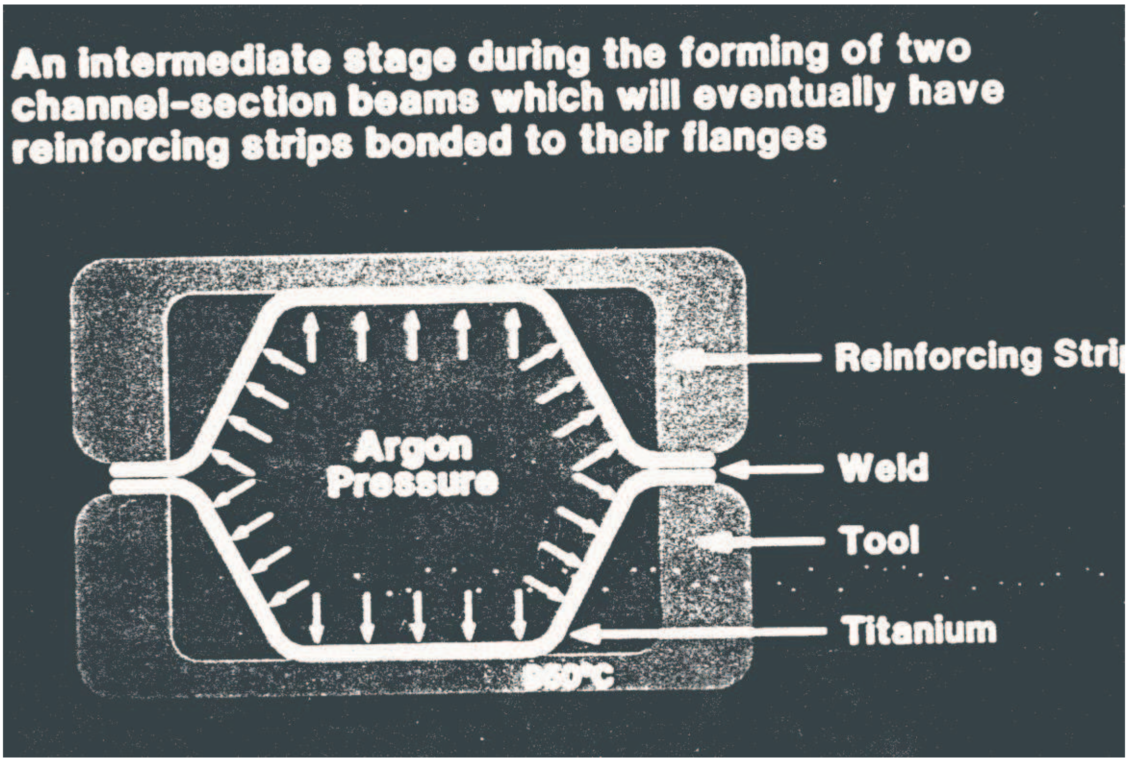
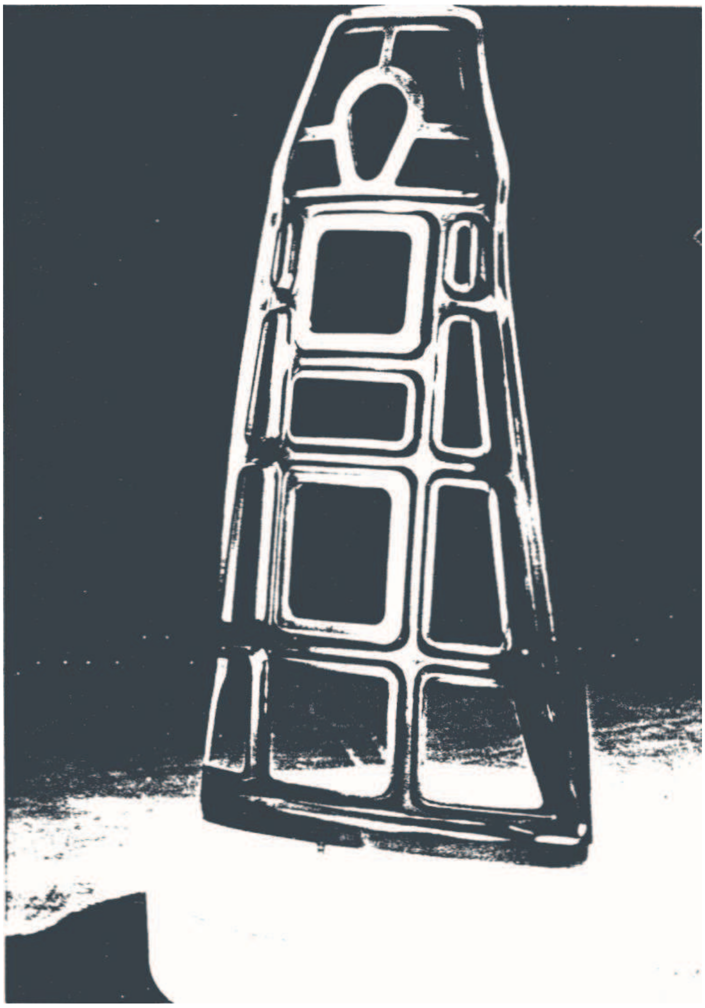


Fig. 30 - A SPF/DB process example

Fig. 31 - SPF part

Fig. 32 - SPF part

Fig. 33 - SPF part



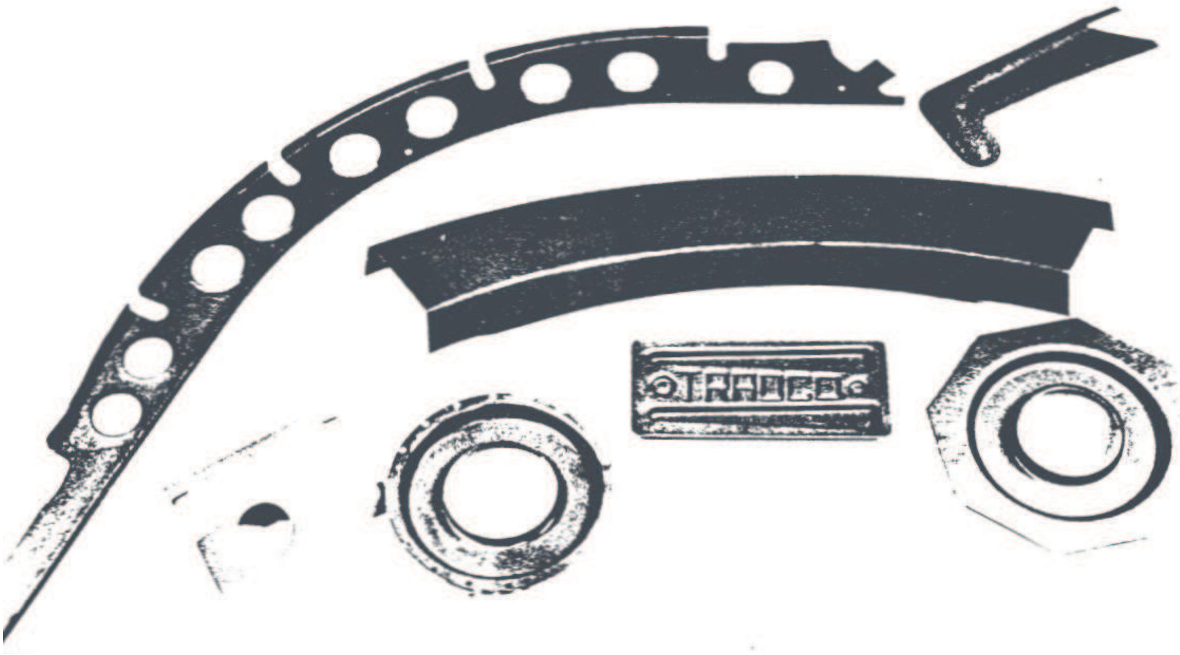
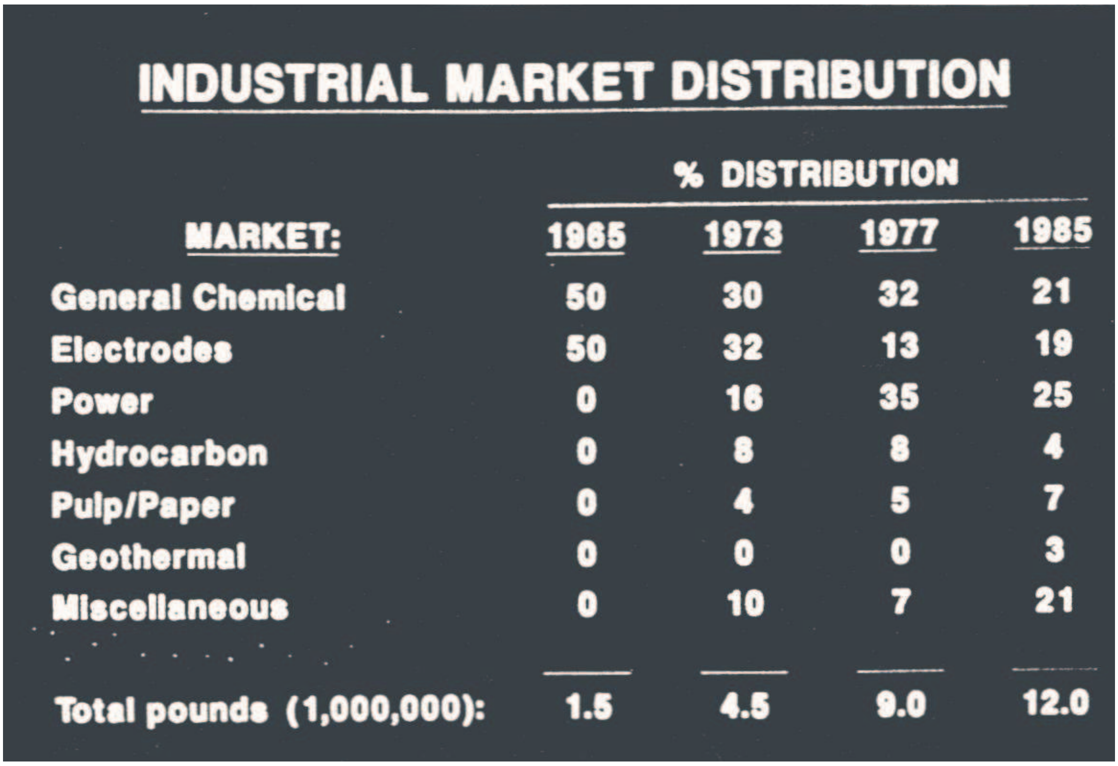


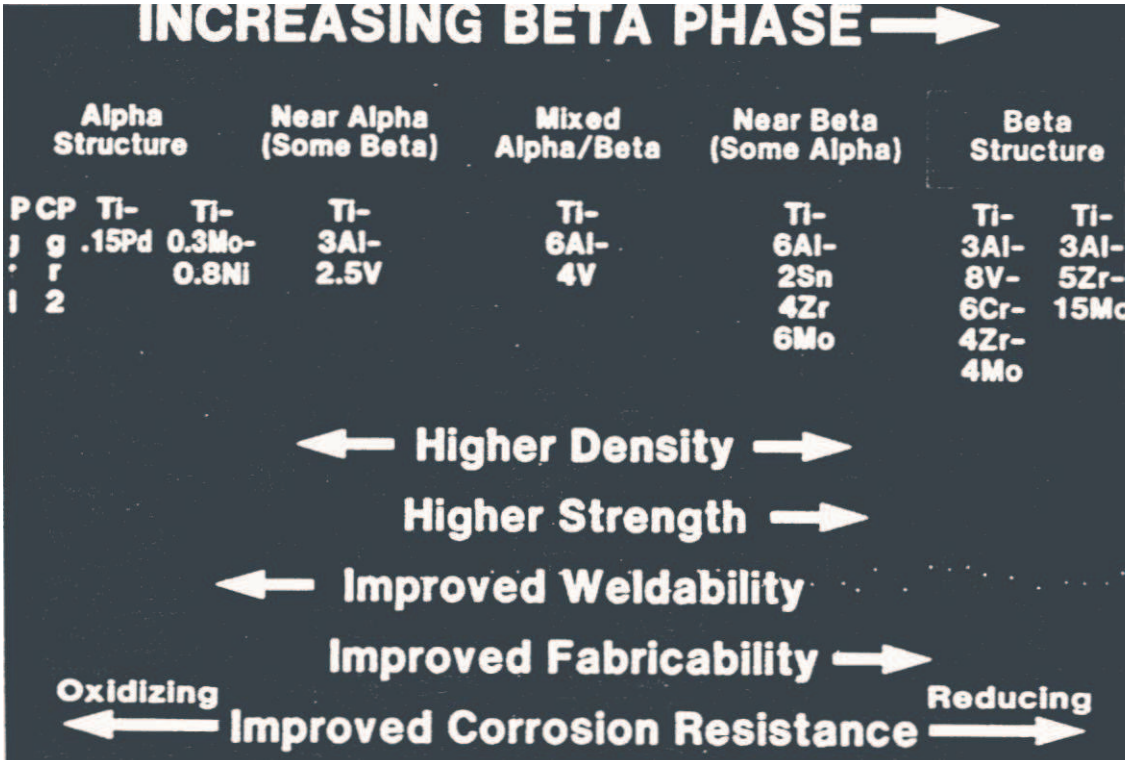
Fig. 34 - Conventional hot formed parts



INDUSTRIAL MARKET DISTRIBUTION

MARKET:	% DISTRIBUTION 1965	1973	1977	1985
General Chemical	50	30	32	21
Electrodes	50	32	13	19
Power	0	16	35	25
Hydrocarbon	0	8	8	4
Pulp/Paper	0	4	5	7
Geothermal	0	0	0	3
Miscellaneous	0	10	7	21
Total pounds (1,000,000):	1.5	4.5	9.0	12.0

Fig. 35 - Distribution and growth of titanium Industrial markets



INCREASING BETA PHASE →

Alpha Structure			Near Alpha (Some Beta)	Mixed Alpha/Beta	Near Beta (Some Alpha)	Beta Structure	
CP g r 2	Ti-.15Pd	Ti-0.3Mo-0.8Ni	Ti-3Al-2.5V	Ti-6Al-4V	Ti-6Al-2Sn 4Zr 6Mo	Ti-3Al-8V-6Cr-4Zr-4Mo	Ti-3Al-5Zr-15M

← Higher Density →

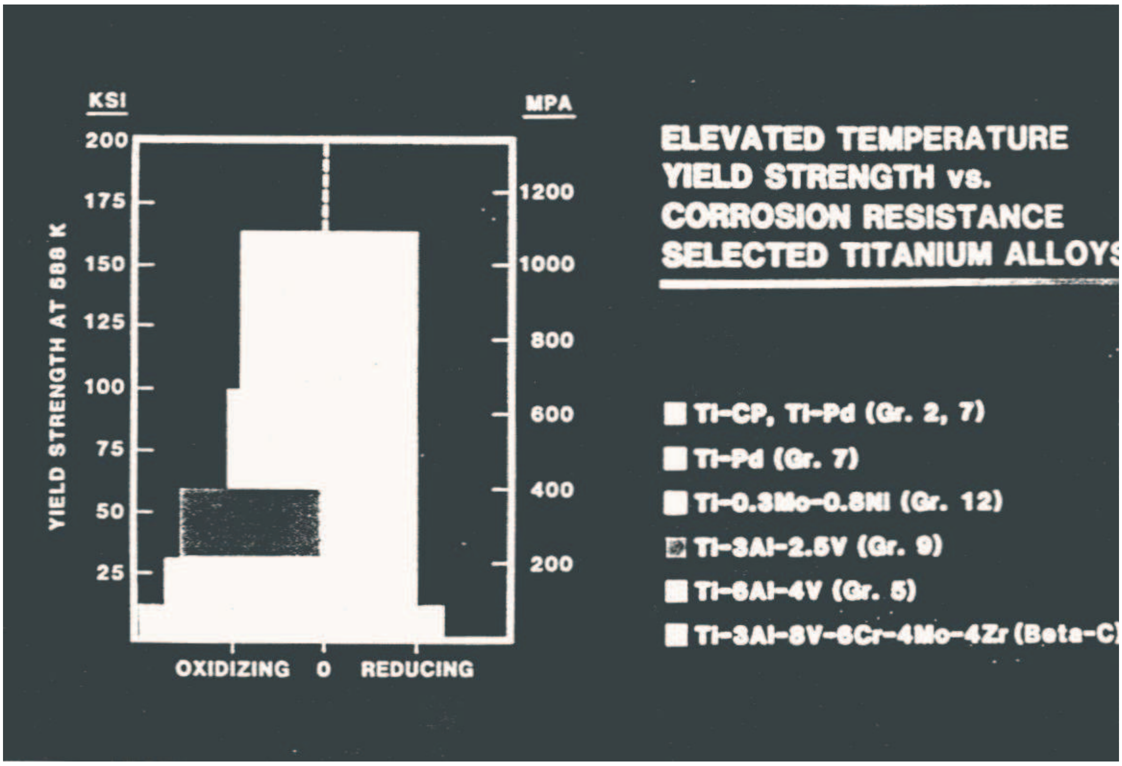
Higher Strength →

← Improved Weldability

Improved Fabricability →

Oxidizing ← Improved Corrosion Resistance → Reducing

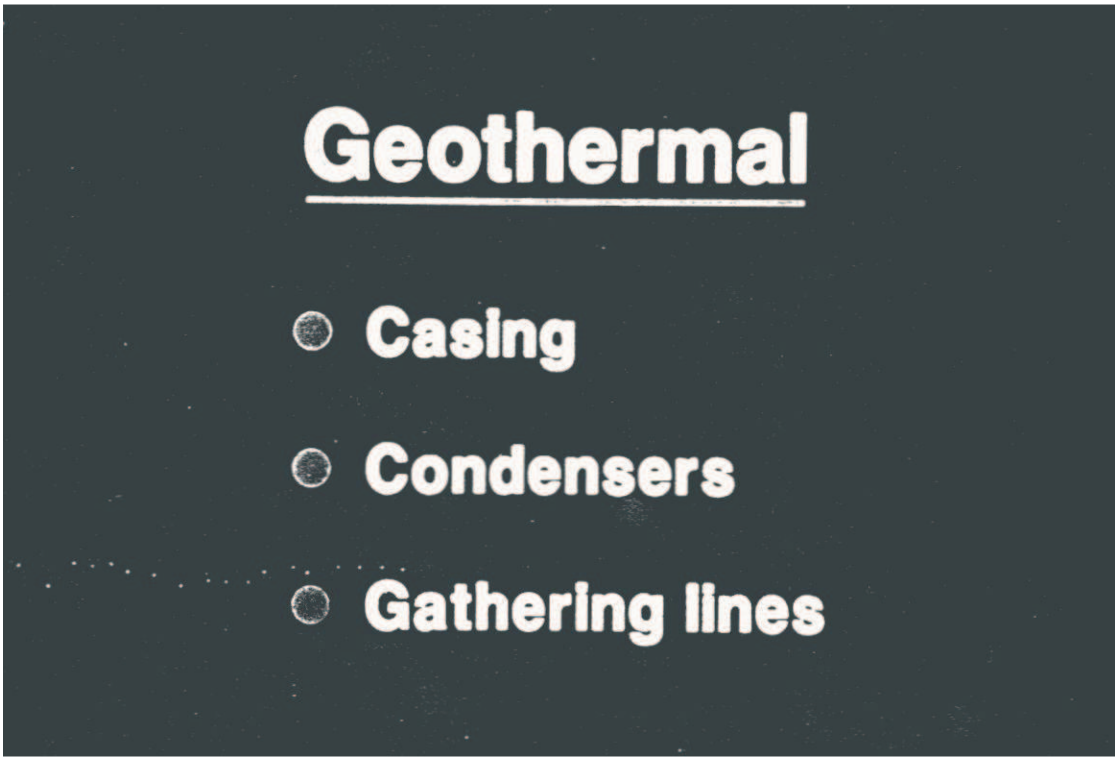
Fig. 36 - General properties of titanium alloys



ELEVATED TEMPERATURE
YIELD STRENGTH vs.
CORROSION RESISTANCE
SELECTED TITANIUM ALLOY

- ■ Ti-CP, Ti-Pd (Gr. 2, 7)
- ■ Ti-Pd (Gr. 7)
- ■ Ti-0.3Mo-0.8Ni (Gr. 12)
- ▨ Ti-3Al-2.5V (Gr. 9)
- ■ Ti-6Al-4V (Gr. 5)
- ■ Ti-3Al-8V-6Cr-4Mo-4Zr (Beta-C

Fig. 37 - Elevated temperature yield strength vs. Corrosion resistance for various titanium Alloys



Geothermal

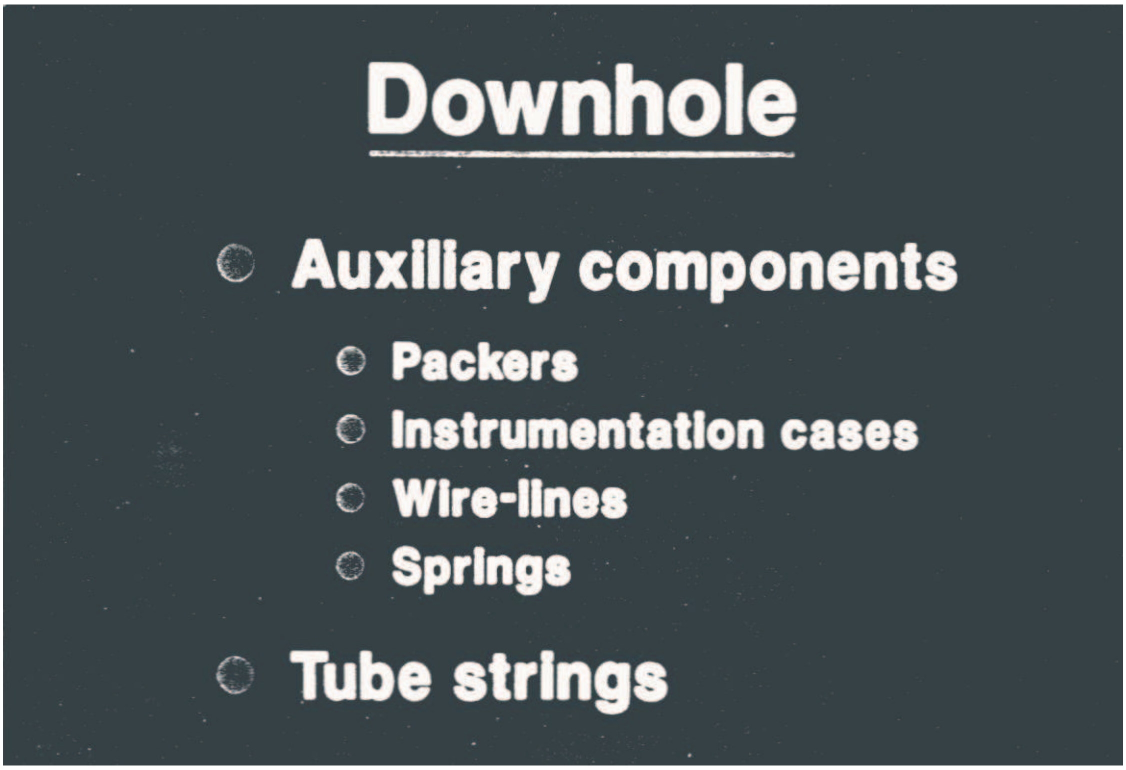
- Casing
- Condensers
- Gathering lines

Fig. 38 - Geothermal applications of titanium alloys

BETA C ADVANTAGES
IN THE
OILFIELD MARKET

1. Heat Treatable
2. High Strength
3. Corrosion Resistance
4. Low Density
5. Low Modulus
6. Hot Workability
7. Geopolitical Stability

Fig. 39 - Beta C advantages in the oil field market



Downhole

- Auxiliary components
  - Packers
  - Instrumentation cases
  - Wire-lines
  - Springs
- Tube strings

Fig. 40 - Examples of downhole applications for Beta C alloy

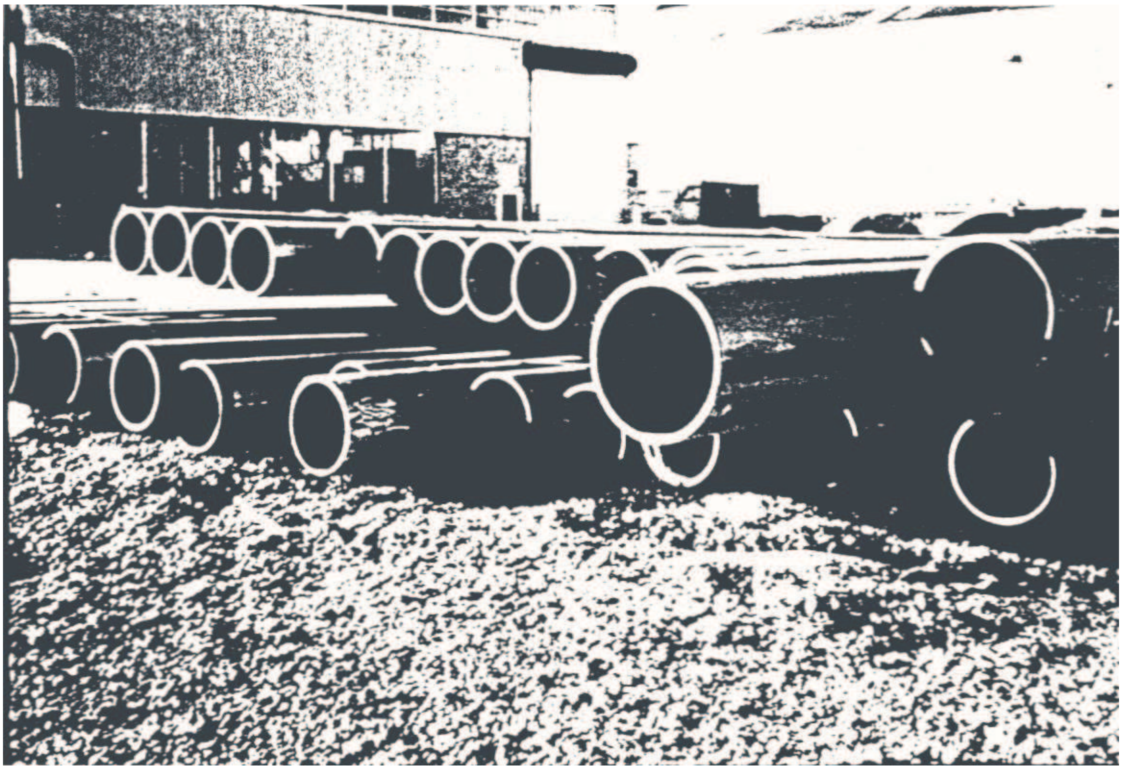


Fig. 41 - Beta C downhole piping

Fig. 42 - Beta C downhole piping

Richard Goosey

IMI Titanium - England

THE IMPORTANCE OF QUALITY IN TITANIUM PRODUCTION

My name is Dick Goosey and I am very pleased to have the opportunity to present a paper to this meeting on behalf of IMI Titanium and in particular Dr. Farthing and Mr. Barber who are unable to be present today. In this presentation I would like briefly to attempt to outline why quality assurance and quality control is so important to the titanium industry and of course to the users of titanium.

In our view the commitment to quality is arguably the most important issue for the titanium industry and we at IMI Titanium operate a policy of nil compromise on quality. What is quality. We believe it is giving the customers the products that meet their specification and technical requirements on a consistent and reliable basis. To achieve this you need to define and operate a Quality Policy which in our experience should focus on

- the customers needs and expectations;
- the need to ensure everyone concerned with manufacture is involved in maintaining quality;
- that all aspects of manufacture from raw materials procurement to final despatch can and do contribute to quality;
- that processes can always be improved. Allied to this is a recognition that regular hazard reviews to identify potential problem areas of the production processes are essential to an ongoing commitment to quality;
- and last but not least, prevention is better and cheaper than cure;

Lack of effective quality control can lead to a non-standard product and in particular and most seriously the formation of material defects the presence of which may lead to very unfortunate consequences.

Against this background let us examine the titanium manufacturing process and identify the important role that quality control plays in ensuring that the final product is to the standard required. In considering the various stages of manufacture I propose to illustrate some of the defects that can be produced in titanium as a result of inadequate quality control. I must stress that the "rogues gallery" of defects I shall show did not all originate in IMI products. They cover a spectrum of producers and represent the types of defect that are seen in titanium from time to time and in varying degrees wherever it is produced.

The process - as shown

Considering first the raw materials. Titanium sponge is produced by high temperature reduction of the tetrachloride by magnesium or sodium. Titanium is a highly reactive metal and the product of the reaction process is therefore susceptible to atmospheric contamination leading to the formation of nitrided/oxidised sponge.

Such contamination is a potential source of the classic Low Density Inclusion (LDI) or High Interstitial Defect (HID) in titanium, known to have been the cause of premature failure in compressor discs of gas turbine aero engines.

Alloy additions in elemental form or as master alloys can also be a source of defects. The Mo inclusion shown illustrates the consequences of adding material in a non-standard form resulting in in-complete solution and the formation of a HDI or High Density Inclusion.

Quality control of all raw materials is therefore vital to successful manufacture of defect free products.

Manufacture of raw materials must be to an approved purchase specification by a manufacturer who has been technically approved by the melter and produces the required product to a fixed method of manufacture agreed with the melter. This combined with regular auditing of the supplier and routine overchecking of the incoming raw material should provide a sound basis in quality terms from which to start manufacture of titanium products.

The ability to recycle scrap effectively is of considerable importance to the titanium producer for cost saving but again control is vital if quality is not to be compromised. In broad terms, recyclable scrap falls into two categories:

- solid scrap - which can be of various types/forms
- machined turnings or chips or swarf

Controls on solids include visual inspection and chemical analysis whilst additional precautions on swarf may include use of WC tool tips bonded with magnetic materials to facilitate extraction of tool fragments during swarf processing and X-ray inspection for WC or any other dense metal inclusions in the processed swarf.

100% X-ray examination of processed swarf is a universal pre-requisite to the recycling of such material into alloys intended for critical aerospace applications.

The consumable electrode arc melting process involves the construction of a primary electrode from raw materials, the stages of construction being blending, mixing, compacting, compact welding.

Quality control is vital at all stages and I would emphasise in particular the control exercised over the compact welding process where contaminated welds are on obvious potential source of interstitially contaminated defects. Visual standards against which welds can be assessed are therefore recommended and applied by IMI.

Electrode integrity or strength is clearly important in ensuring that the electrode is consumed by melting and unmelted pieces do not fall off into the molten pool - a situation which could lead in the extreme to the presence of incompletely melted material within the ingot.

Turning now to the melting process, this must be considered the most important stage in determining the quality of the final product, particularly in terms of freedom from defects.

Furnace cleanliness is paramount and the importance of a disciplined approach to furnace cleanliness cannot be emphasised too strongly. In our view adoption of a rigorous cleaning practice linked to an effective inspection procedure is vital to the consistent manufacture of titanium free from melt related defects.

Combined with this of course is the use of controlled melt schedules to give the control of ingot chemistry required by the customer - the latest and largest furnace installed and operated by IMI Titanium is computer controlled to provide a fully automated melt cycle with its consequence advantages with regard to product consistency.

Most products are double melted and triple melting is now specified for many critical aerospace applications.

Current final melt schedules incorporate a so called hot top cycle to minimise ingot cavity formation and the potential yield loss associated with metal rejection due to the presence of both sealed or unsealed ingot cavity.

The disciplined approach to melting is equally important when considering the subsequent conversion of the ingot to product by thermo-mechanical processing.

Specifications especially for critical aerospace components are becoming increasingly demanding in their requirements for consistently reproducible macro and microstructures and hence properties.

The important controls necessary to meet these objectives cost effectively are listed in the table.

Poor temperature control can lead to unacceptable structures, the most obvious being the totally transformed structure associated with overheating above the beta transus in an operation where the aim is to develop an equiaxed alpha morphology by sub-transus work.

In contrast processing at too low a temperature can lead to surface break up and cracking and internally to the formation of strain induced porosity.

A review of the importance of quality in titanium production cannot overlook the future and in this context the increasing interest in the use of cold hearth melting processes should be mentioned. Potential advantages in terms of eliminating high and low density inclusions during scrap and sponge melting are well documented and I intend only to highlight the developing interest in these processes and their likely importance to the titanium industry in the future.

In summary I hope this brief presentation has given some in-sight into the importance of quality in the titanium industry and will conclude with a reminder of the potential consequences of what a lapse in quality can mean.

Liv Lunde
Institute for Energy Technology -Norway

OFFSHORE USE OF TITANIUM -BENEFITS AND POSSIBLE LIMITATIONS

ABSTRACT

The use of titanium in the oil industry has increased during the last decade. The material is introduced in new and important applications, where full advantage of the excellent corrosion resistance of titanium in seawater and chlorine environments have been taken.

About 100 units of titanium heat exchangers are now ordered or in operation in the Norwegian and the British sector of the North Sea. These include units on the Ekofisk, Albuskjell, S. Eldfisk, Edda, and Maureen platforms, and the Fulmar Field. More than 20 units for hypochlorite production offshore have been installed in the last few years.

The report summarises properties of importance for offshore applications and describes titanium's benefits and possible limitations. The effect of design on the overall behaviour of heat exchangers with special focus on corrosion is discussed. The background for the gradual change from the traditional copper based alloys to titanium in seawater cooled heat exchangers are given. Other offshore applications of titanium is also described and future prospectives for new applications are briefly mentioned. The report concludes with information on availability and prices.

1 - INTRODUCTION

Due to their low density and the high strength even at elevated temperature titanium alloys have been used for a long period by the aerospace industry. About ten years ago titanium entered new applications based on its superb corrosion resistance - reduced price and new industrial processes with aggressive environments, being the main driving force. From 1970 until today the industrial market has grown from about 10% to about 30% of the total world production per year.
The main industrial application of titanium, about 50%, is seawater cooled heat exchangers also components in bleaching plants, for fabrication of acidic acid, and for leaching in strong acids etc has become new applications for titanium, due to its superb corrosion resistance in such environments.

In the offshore industry the dominating application of titanium originates from its immunity to seawater even when badly polluted. Its main application has been in large seawater cooled heat exchangers, especially those operating at elevated temperatures, The traditional material for seawater cooled heat exchangers is copper alloys like cupronickel and aluminium brass. Such materials are very sensitive to certain sulfur containing impurities in the water. Increasing pollution is a motivation to avoid these alloys in some regions.

Compared to the more traditional materials titanium is considered an expensive material. The higher cost can well be balanced by better performance or longer life times. Reduction in weight is also important, when it comes to offshore applications of titanium. Future offshore uses will clearly continue to take advantage of the corrosion resistance of titanium in sea water, chlorinated sea water and sour hydrocarbons, and one can foresee a number of applications which will also take full advantage of the strength to weight ratio of the material.

2 - GENERAL PROPERTIES OF TITANIUM

Different grades and alloys of titanium are available, see Table 1. Unalloyed commercial pure titanium grade 2 is the normal quality in corrosive environments, in contrast to aerospace applications where very strong alloyed alloys, preferably grade S, are being used. In some environments small amounts of alloying additions of palladium, grade 7, or molybdenum and nickel, grade 12, improve the corrosion resistance. The chemical composition of different alloys are given in Table 2a and mechanical properties in Table 2b.

Three grades with different strengths, obtained by varying the oxygen contents are available. The yield strength varies from 170 MPa for the purest one to about 500 MPa for the quality with 0.4% oxygen. Further increase in strength is obtained when other alloying elements as vanadium and aluminium are added. The mechanical properties as given in Fig. 1 are excellent from cryogenic temperature -200°C to 350°C. Above 350°C creep properties must be taken into consideration.

Titanium is a high strength, low density material, density 4.5 g/cm^3, which is 58% of steel. Table 3 shows the relationship between strength and density for three titanium qualities and some other metals it also shows the strength/density ratio for other metals in relation to titanium (3). Stainless steel type 316 has a strength/density ratio of 48% to titanium grade 2 and only 15% to titanium grade 5. Hastelloy C-276 has a ratio of 66% to titanium grade 2 and 21% to grade 5.

The pure titanium qualities and the titanium alloys are standardized in several countries. The most recognized standard is ASTM (American Society for Testing and Materials), giving standards for sheet, tubes, bare etc.

In Table 4 different physical properties of titanium are given in comparison with properties of other materials suited for heat exchanger services. The modulus of elasticity is low, 10400 kg/mm^2, which is about half that of steel, This is inconvenient for structures exposed to deflection and must be taken into consideration. The low modulus is, however, advantageous where flexibility is required.

At high temperature the oxide film dissolves into the metal and reaction with air is rapid so welding must be done in an inert atmosphere. Small traces of air in the welding atmosphere will easily ruin the corrosion as well as the physical properties of the materials. Welding of titanium is treated separately in a special paper at this course (4). TIG welding (tungsten inert gas) with argon or mixtures of argon and helium as shielding gas is a well developed procedure, but requires clean conditions and trained people. It is difficult to fulfil the strict cleanliness specifications if repair welding shall be carried offshore. Repair welding at the platforms has, however, been successfully done by special welders both from Norway and the United Kingdom.

Special workshops for titanium components manufacture exist both in Sweden and Norway. Their dominating market so far has been large components to the paper and pulp industry and seawater cooled heat exchangers.

3 - CORROSION PROPERTIES

3.1 - Aggressive Chemicals

Titanium has high affinity to oxygen and nitrogen and the good corrosion behaviour comes from a passive oxide film formed at room temperature. Unalloyed titanium is highly resistant to corrosion by most natural environments including seawater. Titanium exposed to seawater for many years has undergone only superficial discolouration. Many organic compounds including acids and chlorinated compounds and most oxidizing acids have essentially very little effect on this metal. Titanium is used extensively for handling salt solutions including chlorides, hypochlorides, sulphates, and sulphides as well as wet chlorine and nitric acid solutions. In general, all acidic solutions that are reducing are aggressive to titanium provided no oxidizing inhibitors are added. Fluoride ions in excess of 50 ppm have a tendency to destroy the oxide film and can cause rapid corrosion. In unalloyed titanium weld zones are just as corrosion resistant as the base metal provided that the weld is not contaminated.

Titanium in the passive condition is cathodic to all engineering materials and hence this coupling does not accelerate the corrosion of the titanium, but the other member of the couple. This effect may be important and is treated in some detail below. Active titanium which may occur in reducing environments may suffer increased corrosion by being coupled to other metals, but titanium is not recommended for such environments in general.

3.2 - Aggressive Components in the Hydrocarbons

The hydrocarbons are little aggressive to the common engineering materials, but may contain aggressive constituents - carbondioxide and certain sulphurcontaining compounds being responsible for most severe material problems. The production wells in the North Sea are so far low in sulfur, but an increase with time is normal and wells with aggressive products have already been found. On the British side close to the Norwegian sector a well with a water phase with up to 23 mol% CO_2, 11% NaCl, and 80 ppm S is found. Titanium is highly resistant to sulphidation and pitting in wet H_2S at the temperatures in question, and to sulphide stress corrosion cracking (5). However, there have been cases where titanium has failed in solutions with high H_2S concentrations, probably due to a hydriding mechanism (6). This mechanism has later been demonstrated in lab tests (7).

High amounts of carbon dioxide combined with water in crude oil and natural gas streams lead to some corrosion problems for carbon steel, but this gas has no effect on titanium, whether wet nor dry. Titanium is giving good service in this environment and is being considered for riser- or production pipes for very aggressive wells in other parts of the world.

3.3 - Seawater

Both in seawater and in sodium chloride brines, is commercially pure titanium immune to all types of attack up to certain temperatures depending on salt concentration. Fig. 2 clearly demonstrates the area of complete immunity. In seawater this is up to approximately 130°C. Above this temperature attack has been observed under tight teflon gasket under process scales, or under special conditions with unfavourable packing design, low pH and stagnant conditions. At lower temperatures titanium is unaffected by stagnant seawater. Above about 150°C, in seawater, and at lower temperatures in brines of higher sodium chloride contents, pitting attack may take place, dependent to an extent on the pH of the environment and the extent of contamination. Titanium with 0.15% Pd is immune to crevice and pitting corrosion at temperatures up to 30°C or 40°C in excess of the safe limit for commercially pure titanium. It should be noted that the temperature referred to relates to the metal temperature in contact with the brine or seawater.

3.4 - Erosion Corrosion and Fouling

For film covered metals in general there is a critical water velocity above which the corrosion film is damaged by the water flow and accelerated corrosion occurs. For copper alloys this critical velocity is in the range of less than 3 meters per second while titanium and stainless steels tolerate flow rates more than 20 m/s as seen from Fig. 3 (8). Such high flow rates are hardly used in practice due to high pump energy consumption. Normally the corrosive metal loss is negligible and no corrosion allowance is added in design.

While stagnant seawater can be disastrous to copper based alloys due to pitting with following erosion attack, titanium can take stagnant seawater for long periods. Titanium shows little toxic effect towards micro organisms and some fouling is expected to occur in static water. However, there has been no evidence of any crevice or deposit attack beneath the growths and they can normally be easily eliminated by chlorine injection or sponge hall cleaning (9). The effect of water velocity and sponge hall cleaning on fouling of titanium tubes are shown in Fig 4. (10). Titanium also offers good resistance towards particle erosion, see Fig. 5. It is seen that additions of up to 15 g/l sand has a significant effect on the corrosion of copper alloys in seawater, while titanium is uninfluenced by the same additions (1). Hawaiian Electric Power was in 1982 replacing turbine condensers of unit 1 to 6 at Kahe Termal Power Plant to titanium in order to prevent erosion by sand and coral pieces (29).

3.5 - Galvanic Corrosion

Heat exchangers have often been made with tubes of titanium while other materials have been used in tube-plates, baffles, water, boxes etc. The possibility for accelerated anodic dissolution of the less noble metal must be carefully evaluated when titanium is used in direct contact with other metals.

Fig. 6 shows the behaviour of titanium and dissimilar metal couples at different anodic-cathodic area ratios (11). The importance of the ratio of surface area is seen. Only when the surface area of titanium is high compared to that for the anodic material significantly increased corrosion occurs. This is discussed in some detail in a later section.

3.6 - Hydriding

Atomic hydrogen may be absorbed by titanium during corrosion (similar to what is happening to steel in H_2S environments). If the solubility limit is exceeded (roughly 20 ppm at room temperature) titanium hydride is formed. In extreme cases large platelets are formed or the metal is transfered completely into the brittle titanium hydride.

Hydrogen can be formed by corrosion of titanium itself, or by corrosion of another less noble metal which is galvanically coupled to titanium. The latter process if often occuring in narrow crevices between two dissimilar metals. Hydrogen formed at the anode will diffuse through the oxide film of the cathodic titanium. Titanium will have a less protective oxide film under the reducing conditions in a crevice.

Hydriding must not necessarily be a result of corrosion, it can also occur with applied current cathodic protection of a less noble metal. It is seen from Fig. 7a that a rapid increase in hydrogen absorption occurs at a voltage more negative than -700mV /vs. sat calomel (9). Heavy hydrides were formed in a heat exchanger in Japan as a result of cathodic over-protection (7,10). The absorption of atomic hydrogen is much dependent upon temperature. The absorption is insignificant at room temperature, but increases rapidly at temperatures above 100°C (5). Penetration and diffusion of molecular hydrogen do not occur at significant rate until excess of 250°C.

The presence of an oxide film either by thermal oxidation or by anodizing will protect against introduction of hydrogen as seen from Fig. 7a. Thermal oxidation in air at temperatures below 400°C has also been used as surface protection. However tests in the IMI Titanium laboratories lasting over 3 years show that the benefit does not last. In the long term there was no difference in the rate of hydrogen uptake for titanium with a pickled surface or an anodically oxidized surface as shown in Fig. 7b. A temperature increase from 20°C to 60°C will lead to a significant increase in hydrogen absorption, Fig. 7c (12).

3.7 - Stress Corrosion Cracking

Titanium and titanium alloys are generally considered to have a high resistance to stress corrosion cracking. Stress corrosion cracking may, however, occur in methanol, red fuming nitric acid and chlorinated hydrocarbons. In seawater the stress corrosion resistance of titanium and titanium alloys in general is very good. It is, however, reported that a few titanium alloys are susceptible to stress corrosion when immersed in seawater under highly stressed conditions (13).

4 - HEAT EXCHANGERS

4.1 - Plate and Shell-and-Tube Type Exchangers

The main application of titanium in offshore hydrocarbon production has been heat exchangers. Approximately 30 plants are now operating in the North Sea with about 100 units of shell and tube exchangers. With an estimate of 45 operating plants in 1990, it will be a market for 50 to 60 units of titanium heat exchangers for the years 1984-1990 (14). With an assumed average of 250 m^2 heat transfer area per unit, this means 12500 - 15000 m^2 in all (3).

Two different design concepts are used for heat exchangers: the plate type and the tube type. Per unit area of heat transfer surface, the plate type heat exchanger is the cheapest one, but this concept can not tolerate high pressures. For high pressure systems two seawater cooling concepts are used, the direct one with tube heat exchangers - or the indirect one, where a central plate heat exchanger with seawater cooling, cools an intermediate fresh water circuit, which in its turn is fed to a process heat exchanger of the tube type made of cheaper material.

Plate heat exchangers of titanium have been widely used for offshore duties on production platforms and also for compressor cooling and direct low pressure crude oil services (15).

We have been informed that central plate heat exchangers are still ordered for the platforms in the North Sea, while other operators previously using indirect systems are planning to use direct cooling on future projects.

4.2 - Problems with Galvanic Coupling

The tube plate, the shell and the baffles are for most applications made of more cheap materials than titanium. Aluminiumbronze, stainless steel, or stainless steel clad carbon steel can be used for tube plates in the uncoated conditions, while Munz metal, naval brass, and cupronickels are preferred coated either by rubber or epoxy. Exxon reports excellent behaviour of monel clad carbon steel in more than 50 heat exchangers in U.S. (16).

Nickel aluminiumbronze is very much more compatible with titanium in seawater than other materials, as seen from Fig. 6. IMI reports that Mobil Coryton refinery has used 10.000 m tube installation with no sign of galvanic attack after 36 months' operation. Furthermore, small drain cooler units tubed in titanium into nickel-aluminiumbronze tube plate also showed no sign of attack when 70/30 cupronickel was attacked after 24 months' service (5). 1t should be noted that the name aluminiumbronze covers different groups of alloys with different behaviour when coupled galvanically to titanium. Qualities with aluminium as the only alloying addition will in general give a significantly poorer service than the qualities which also have additions of nickel and iron (5).

When it comes to water boxes both aluminiumbronze and carbon steel have been used, the first unprotected while the latter one must be coated or cathodically protected by soft iron anodes.

Special care must be taken when aluminiumbronze is used as tube plate together with coated ferrous water boxes. Small defects in the protected layer on the water box may then lead to rapid deterioration of the carbon steel due to the galvanic effect of the large cathodic aluminiumbronze area.

Typical North Sea conditions are inlet temperature of up to +9°C, outlet temperature 16-27°C, flow rate 3-6 m/sec. The shell side has a mixture of oil and gas in varying proportions. Inlet temperature is 100-200°C, outlet around 20°C, flow rate 3-6 m/sec (17). More detailed information on the environmental conditions for heat exchangers installed by one operator is given in Table 5 (18). Crevice corrosion problems and tube cleaning are most easily handed by using the seawater on the tube side, and this is regarded as the normal practice. Six out of the seven different types of coolers referred to in Table 5 used the traditional concept with seawater tube side and product shell side, with the large discharge coolers as the only exception. Due to the high pressure of the hydrocarbons, seawater at the shells side was selected in this case. The temperature was 100-110°C.

Four of these large coolers installed in 1976 suffered severe damage to baffles and shell after about four years’ operation. The reason was mainly caused by an action of galvanic corrosion of the nickel-free aluminiumbronze baffles due to the contact with titanium. The galvanic attack was enhanced by the large surface area of the titanium tubes, this area being 17 times larger than the Al-bronze area. Unproper baffle design may also have contributed to the attack. As a consequence of the loss of the integrity of the baffles, the titanium tubes started to vibrate, which in its turn caused fatigue failures of the tubes. Even the vessel of aluminiumbronze was destroyed locally due to fretting caused by contact with vibrating tubes. The Monel clad tube plate was in good condition (26).

The operator replaced their heat exchangers and used at that time a titanium clad steel sheet plate, titanium baffles, and titanium shell. Difficulties were nevertheless also experienced with these new exchangers. The tubes in the U-bend bottom part of the exchanger were not sufficiently supported by baffles and the particular shell construction led to high flow velocities in this part of the exchanger. The exchangers failed once more after a few years operation - this time due to tube vibration. The heat exchangers are at the time being rebuilt in England. The bottom part of the shell is lengthened and the number of baffles in the U-bend part are increased.

The difficulties experienced with these exchangers examplifies the two main concerns that have to be taken into account when using titanium. Possible galvanic action between dissimilar metals have to be evaluated and consideration to the low E-modules must be taken. It should be stressed that these failure cases have been exceptions. About 100 heat transfer units have been installed in the North Sea, and we are not aware of serious difficulties with other exchangers. It should be remembered that the expansion in the North Sea has been so fast and the total projects so large and complicated that some mistakes may be unavoidable.

4.3 - Tube to Tube Plate Sealing

Titanium can not be welded to other materials. Thus, welding of tubes to the tube plate can only be achieved if the tube plate is of titanium or coated with titanium. The latter design is most commonly used - the titanium layer normally being applied by explosion coating. Normal cladding thicknesses are about 10 mm. Both manual and automatic TIG welding (tungsten inert gas welding) is used with argon or mixtures of helium and argon as the protecting gas. In order to prevent the metal from flowing away a pulsed current, allowing the metal to solidify at intervals, is normally applied. Welding is not regarded as specifically difficult, but the cleanliness requirements, and the high number of welds (up to 50.000) make such production a task for special firms.

Rolling in tube to the tube plate is done by standard techniques with three or five rolls under torque control. As titanium has a low modulus of elasticity and is unisotropic (due to the hexagonal structure) optimum rolling in conditions must normally be tested out with the same tube plate materials and tubes as those to be used.

Plastics with good stability at moderate temperatures exist. In some cases a special plastic lacquer has been applied to improve the sealing between the tube and the tube plate. This approach is very interesting because the crevice between the tube and the tube plate is in principle a weak point in the design.

4.4 - Vibration and Fatigue

In most applications titanium is used with thinner wall thicknesses than other materials due to its excellent corrosion resistance. This combined with a low modulus of elasticity lead to little stiffness and low resonant frequences for vibrations. The space between the tube supports used for titanium tubes must be shorter than for copper or stainless steels.

The conventional support of tubes is segmented baffles where the tubes are thread through holes in the plates. A new design, so-called rod baffles, with spacer rods stuck in between the tubes introduced by a U.S. oil company, is interesting because the more uniform flow allows one to up-grade the heat rating (15).

The rods provide 4-point confinement of the tube to eliminate tube vibration and possible tube failure. The rods are connected to a larger support ring positioned around the tube bundle. The improved flow dynamics result in lower pressure drop, low fouling rates and easier cleaning. new exchangers are designed with appropriate spacing usually about 0.8 m for 0.7 mm tubes when segmental baffles are used and 0.15 m for rod baffle design. Retubing existing heat exchangers with titanium will normally involve installation of additional baffles, which can be difficult and expensive. In many cases a butyl rubber strengthening system has been used instead (15).

4.5 - Heat Transfer

The copper-based alloys are known for their good heat transfer which is much higher than for titanium, see Table 4. It must be remembered, however, that much thinner walls can be applied when titanium is used. The thinner wall can, however, not fully compensate the poorer thermal performance. According to calculations and laboratory tests, titanium condensers have a poorer thermal performance than one made from aluminium brass. Practical experience has shown that the opposite often is the case. The thermal conductivity is gradually reduced due to oxide and layers from the $FeSo_4$ dosage which is used for protection of the copper alloy. Heat transfer reductions of 70% have occasionally been found. New aluminium brass condensers in Sweden had an overall heat transfer of roughly 3200 $W/m^2°C$, but after some years with $FeSo_4$ dosage and sponge ball cleaning this had decreased to 2400 $W/m^2°C$. Measurements performed on titanium condensers have given values about 3100 $W/m^2°C$ at the same cooling conditions, but with unlimited sponge ball cleaning. In the case of copper alloys this cleaning has to be restricted due to these materials poorer erosion corrosion resistance (19).

Experience in Japan from a titanium tubed seawater cooled power station showed that the heat transfer coefficient of 0.5 mm thick tubes was only reduced 3.5% after 27 months' of operation which is much less than what is experienced with copper-based tubes (5).
Swedish experience from nuclear reactors are similar. Titanium had a much better heat transfer after 14 months operation compared to Albrass tubes (20).

Low finned titanium tubing with plain bore has been introduced lately. These tubes provide good heat transfer performance combined with good corrosion behaviour. Exxon informs that such tubes are installed in oil refinery heat exchangers in U.S., but no details on their performance is given (16).

5 - COMPARISON WITH TRADITIONAL MATERIALS FOR HEAT TRANSFER

The traditional material for seawater cooled heat transfer is copper alloys like aluminiumbrass and cupronickel. For these copper alloys the critical velocity before erosion corrosion occurs, is a few meters per sec in seawater, as shown in Fig. 3. This critical velocity may be drastically reduced if the water is polluted, especially are some sulfur containing constituents harmful. Nor can the copper alloys except stagnant water for long periods. Due to the general increase in pollution it is not surprising that copper alloys which earlier exhibited sufficient corrosion resistance have suffered an increasing amount of damage. McMaster has collected data from oil refinery heat exchangers in U.S. which previously used copperbased alloys or standard stainless steels before changing to titanium. Table 6 gives a view on the conclusions on failure mechanisms drawn from the more than 60 case histories conditions where titanium behaved satisfactory. Common for the copperbased alloys are sulphidation on the process side and denickelfication on the water side. Zink-containing alloys as admiralty brass suffered from dezinkification in the cooling water (6).

Tubes of copper alloys in a high number of condensers for power plants both in England, Sweden and USA have given problems and the condensers have been retubed with titanium. See Table 7. The experience with copper based tubes in the Swedish nuclear power plants is far from encouraging. Twelve of the sixteen condensers with tubes of aluminium brass installed before 1977 have been retubed with titanium due to corrosion damage, two of them after only 3 years' duty, see Fig. 8.

After a 10000 hours' exposure period, corrosive attack penetrating more than 60% of the tube walls was detected for a percentage of the tube varying between 1 to 4.5%. In the condensers of the Barseback reactor operating with a salinity (12 g NaCl/l) a wall reduction as high as 80% was found. One condenser in Ringhals with tubes of CuNi 90/10 was retubed with titanium after one year only. With respect to heat exchangers with titanium tubes no leakage is so far detected and when the condenser in the Ringhals II reactor was examined after four year's operation, no attacks was observed at all.

6 - OTHER ESTABLISHED OFFSHORE APPLICATIONS FOR TITANIUM

6.1 - Hypochlorite Lines

Hypochlorite solutions are needed for different purposes on a production platform. This if often produced in electrolytic hypochlorite generators onboard. Titanium is completely resistant to hypochlorite solutions and is most suitable for such process systems. Today more than twenty systems with titanium are installed in the North Sea.

Most of them were replacements for PVC installations which lacked necessary impact and fatigue strength, but at least two were installed as original equipment and this trend will continue (21).

Hypochlorite solutions are also used for treating of water for reinjection in production wells. Titanium is used to some extent for such watertreatment systems in pipes, valves, pumps and tanks.

6. 2 - Data Logging

About 100 tonnes of titanium are used annually for the internal mechanical components and encapsulation of data loggers. Most is in the form of bar and thick wall pipe in Ti-6Al-4V.
This alloy is chosen for its high strength and low density, non-magnetic properties and corrosion resistance in the hot, high sulphide and chloride conditions down-hole (22).

6.3 - Submersibles

Titanium is being used for structures, pipework and pressure spheres in deep submergence vehicles, and is unrivalled for depths below 2000 m. The high strength/density ratio and corrosion resistance may well have advantages for much shallower work (22).

6.4 - Portable Compression Chambers

Titanium is already used for diver rescue chambers for one or two men. Current developments relate to the use of higher strength titanium alloys to provide larger lighter chambers to evacuate a whole team (22).

6.5 - Fire Services

Titanium pipework, seamless up to 150 mm or fabricated from plate for larger diameters is being considered for these critical duties on rigs and platforms. It is already in use on fire-boats (22).

6.6 - Tanks and Bottles for Chemicals and Samples

An increasing variety of containers for bringing pressurized oil/gas product samples ashore for analysis, and for safe transport of chemicals to offshore installations, is becoming available in titanium.

Other offshore applications of titanium are hydrofoil parts, anodes for cathodic protection, exhaust gas scrubbers, and propeller shafts.

7 - POSSIBLE FUTURE APPLICATIONS OF TITANIUM

7.1 - Sub-sea Production

Deep seawater production of hydrocarbons will require other solutions for production equipment than in shallow waters. The exclusion of maintenance by divers will require more reliability and longer working life. Titanium can be a solution for many problems connected to subsea hydrocarbon production.

Chemical injection, chemical dosing and seawater distillation are also areas where titanium may come in.

7.1.1 - OTEC

Ocean Thermal Energy Conversion process (OTEC) utilizes naturally occuring temperature gradient found in the ocean to produce usable energy. The main criteria for selections of materials to commercial OTEC plants will be:

- Low overall cost (initial cost and maintenance or repair costs) for a lifetime of 30 years.
- Reliability in seawater/working fluid environments (typical ammonia).

Commercial pure titanium (grade 2) is the leading candidate for OTEC heat exchanger tubing, but with a strong challenge from super-stainless steels. Since the overall cycle efficiency is low, the heat exchangers must be large. OTEC represent for this reason a considerable perspective application for titanium tubes. Also piping, valves, turbines, pumps and ducts represent perspective applications of titanium in the OTEC process. AMR, a Norwegian engineering company, Institute for Energy Technology, Kvaerner Brug A/S and Ing. F. Selmer have designed an OTEC plant based on the use of titanium (23).

7.1.2 - Marine Risers

A feasibility study on a complete titanium riser array has indicated a complete system cost just twice that of the equivalent steel array. The system comprised 445 mm bore 13 mm wall thickness risers longitudinally welded from roll formed plate with associated seamless extruded kill and choke and booster tubes 89 mm bare and 10 mm wall thickness designed for a 3000 m water depth.

The exercise established the existence of applicable technology in fabricating marine risers in titanium, where weight saving is vital to maintain the stresses in a riser within acceptable limits as the drillship heaves. The light weight and corrosion resistance of titanium will permit drilling in water depths of over 1800 m.

A large Japanese project has developed a removable “Subsea Production System” for deep waters without the use of divers or guidelines. The lower part of this re-entry riser has been made from titanium. The largest bending moment occurs in this bottom section so titanium is used on account of its high yield strength, low E-modules, good fatigue properties and corrosion resistance (24).

7.1.3 - Riser Stress Joints

The above mentioned properties has led to the development of tapered hollow Ti-6Al-4V riser stress joints. A 3/10 scale model has been extensively tested. Pre-stressed riser connectors in titanium similarly reduce weight and increase fatigue life (22).

7.1.4 - Product Flow Lines

The corrosion resistance and comparatively low modulus of titanium with its high fatigue strength lead to a number of possible applications as flexible flow line elements in novel production systems for small reservoirs or deep water (22).

8 - AVAILABILITY

Titanium is blessed with abundant resources. It is the fourth most abundant metal in the earth’s crust, after aluminium, iron and magnesium. Estimates of resources for titanium vary widely, but all sources confirm that they are great. Data from U.S. Bureau of Mines gives a total of 770 million tons titanium available (Lynd 1978). Fig. 9 gives the world production of titanium in comparison with aluminium and magnesium. It is seen that the world production which started about 1950, in 1980 has reached about 100.000 ton (25). The total world titanium metal capacity for 1984 was 180.000 tons while estimated consumption was 130.000 tons (3). Production of titanium metals require more energy than production of other metals. Electrolytic production of titanium is experimentally developed and a successful method is estimated to reduce energy consumption with 40%. Powder metallurgy may alBo reduce cost for certain applications of titanium in the future.

9 – PRICES; INITIAL EXPENDITURE VS. CAPITALIZED COSTS

The prices of titanium has decreased over the years compared to other materials except for one coincidence. In the end of 1970’s it was a great demand for titanium to aerospace industry simultaneous with an embargo of titanium from USSR. This raised the prices considerably, but due to capacity increase, the prices are now back to old levels, inflation taken into account.

Fig. 10 shows the price development in Germany for some mill products from 1974 to 1983. The price decrease indicated after 1982 is now levelling out and prices are at the time being not too different from that experienced in 1983.

In Table 8 we have compared prices of typical seawater resistant materials. Since titanium is a light metal it is important to compare prices on a volume basis and not on a weight basis as often done. Most people are not aware that the difference in material prices for titanium are only marginal to high molybdenum stainless steel for instance. Table 9 gives prices of typical heat exchangers tubes in titanium, a ferritic stainless steel and an austenitic steel. The austenitic stainless steel 254SMO has been chosen for the main seawater systems at Gullfaks A. It is worth while observing that the cost of titanium is only 10-20% higher than the costs of this advanced stainless steel. Fabrication costs are about equal for these two materials.

Price evaluations are often based on initial expenditures rather than capitalized costs over a full life time. Such calculations can be very misleading in cases where maintenance and production shut-downs are detrimental for the overall economy. Great similarities exist between a nuclear power station and an offshore platform, as in both cases production stops can mean considerable capital loss.

Fig. 8 shows the history of nuclear power plant condensors in Sweden and Finland over the few past years - the average condensor life span has been approximately 6.5 years. It is obvious that a minimum of 4 retubings during the 30 years life time of a power plant must be taken into account. The result of an economical calculation for a power plant with Aluminium brass vs. titanium condensors is given in Table 9. The Albrass alternative is 50% more expensive than the titanium alternative. It is seen that the difference in favour of titanium is about 90 MNOK.

Availability, production capacity and possible reduction of production prices indicate that titanium prices shall be no obstacle to expansion of titanium applications in offshore hydrocarbon production. Today the difference in material prices are only marginal to high molybdenum stainless steels. As manufacturers production capability exist, the expansion in the use of titanium will be dependent on to what extent consulting engineers and design engineers are able to acquire knowledge about this amazing material. To some extent the expansion also will be dependent on the ability to pay attention to overall cost instead of initial expenditure and a1so to what extent field operaters are able to overcome conservatism.

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TABLE 1. DIFFERENT GRADES OF TITANIUM ALLOYS

ASTM GRADE	CHARACTERISTICS AND TYPICAL APPLICATIONS
1	Unalloyed titanium with low strength and high ductility. Often used for lining of heat exchanger tube plates.
2	Most common unalloyed titanium used for corrosion resistant equipment. Optimized combination of strength, welding, and forming characteristics.
3	Unalloyed titanium with oxygen additions to increase strength. used in heat exchanger tube plates.
5	High strength titanium developed for aircraft and space industry.
7	Alloying with 0.2% Pd has given improved corrosion resistance, particularly in reducing environments. Same strength as grade 2.
9	Good corrosion properties and increased strength at elevated temperatures.
12	Alloy with 0.8% Ni and 0.3% Mo with increased corrosion properties compared to grade 2 and considerably cheaper than grade 7. Increased strength at elevated temperature compared to grade 2.

Most of the data reported in the present report is referred to grade 2.

Titanium grades 4, 6, 8, 10 and 11 are also available (see Tables 2a and 2b), but these are less commonly used compared to the alloys listed above.

TABLE 2a Chemical Requirements

Element	Composition, %									
	Grade									
	1	2	3	4	5	6	7	10	11	12
Nitrogen, max	0.03	0.03	0.05	0.05	0.05	0.05	0.03	0.05	0.03	0.03
Carbon, max	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.08
Hydrogen,[A] max	0.015	0.015†	0.015	0.015	0.015	0.020	0.015	0.020	0.015	0.015
Iron, max	0.20	0.30	0.30	0.50	0.40	0.50	0.30	0.35	0.20	0.30
Oxygen, max	0.18	0.25	0.35	0.40	0.20	0.20	0.25	0.18	0.18	0.25
Aluminum	...	...	...	...	5.5 to 6.75	4.0 to 6.0	...	...	...	...
Vanadium	...	...	...	...	3.5 to 4.5	...	...	...	...	...
Tin	...	...	...	...	...	2.0 to 3.0	...	3.75 to 5.25	...	...
Palladium	...	...	...	...	...	...	0.12 to 0.25	...	0.12 to 0.25	...
Molybdenum	...	...	...	...	...	...	...	10.0 to 13.0	...	0.2 to 0.4
Zirconium	...	...	...	...	...	...	...	4.50 to 7.50	...	...
Nickel	...	...	...	...	...	...	...	...	...	0.6 to 0.9
Residuals[B,C] (each), max	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Residuals[B,C] (total), max	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Titanium[D]	remainder	remainder	remainder	remainder	remainder	remainder	remainder	remainder	remainder	remainder

[A] Lower hydrogen may be obtained by negotiation with the manufacturer.

[B] Need not be reported.

[C] A residual is an element present in a metal or an alloy in small quantities inherent to the manufacturing process but not added intentionally.

[D] The percentage of titanium is determined by difference.

† Editorially corrected.

TABLE 2b Tensile and Bend Requirements

Grade	Tensile Strength,[A] min		Yield Strength,[A] (0.2 % Offset)				Elongation in 2 in. or 50 mm, min, %	Bend Test[B]	
			min		max			Under 0.070 in. (1.8 mm) in Thickness	0.070 to 0.187 in. (1.8 to 4.75 mm) in Thickness
	ksi	MPa	ksi	MPa	ksi	MPa			
1	35	240	25	170	45	310	24	3T	4T
2	50	345	40	275	65	450	20	4T	5T
3	65	450	55	380	80	550	18	4T	5T
4	80	550	70	485	95	655	15	5T	6T
5	130	895	120	830	...	...	10[C]	9T	10T
6	120	830	115	795	...	...	10[C]	8T	9T
7	50	345	40	275	65	450	20	4T	5T
10[D]	100	690	90	620	...	...	10[C]	6T	6T
11	35	240	25	170	45	310	24	3T	4T
12	70	483	50	345	...	...	18	4T	5T

[A] Minimum and maximum limits apply to tests taken both longitudinal and transverse to the direction of rolling. Mechanical properties for conditions other than annealed or plate thickness over 1 in. (25 mm) may be established by agreement between the manufacturer and the purchaser.

[B] *T* equals the thickness of the bend test specimen. Bend tests are not applicable to material over 0.187 in. (4.75 mm) in thickness.

[C] For Grades 5, 6, and 10, the elongation on materials under 0.025 in. (0.635 mm) in thickness may be obtained only by negotiation.

[D] For material in the solution treated condition.

Table 3 Comparison of strength/density ratio for titanium/titaniumalloys and some other materials. (3)

Material	Yield strength at 20°C min MPa	Density g/cm^3	Strength/ density ratio	In relation to Ti Gr.2 %	In relation to Ti Gr.5 %
Titanium Gr.2	275	4,51	61	100	32
Titanium Gr.5	830	4,42	188	308	100
Titanium Gr.12	345	4,43	78	128	41
Aluminum B51S-WP, NS 17305	300	2,70	110	180	59
Stainless steel 13 % Cr, AISI 410	350	7,72	45	74	24
Stainless steel AISI 316	230	7,94	29	48	15
Stainless steel Duplex (SAF 2205 ∿ ASTM A 669)	450	7,80	58	95	31
Stainless steel high molybdenum (254 SMO)	300	8,00	38	62	20
Monel 400	175	8,83	20	32	11
Inconel 625	415	8,44	49	80	26
Hastelloy C-276	355	8,89	40	66	21
Cupper/Nickel 70/30	120	8,90	13	21	7

Table 4. Physical Properties of Condenser Tube Material /26/.

Material	Density at 20 °C (g/cm^3)	Coef. Thermal Expansion 20-300 °C (x10^{-6} °C)	Thermal Conductivity at 20 °C (cal-cm/cm^2.sec.°C)	Modulus of Elasticity (kg/mm^2)	Yield Strength (kg/mm^2)	Tensile Strength (kg/mm^2)	Elong. %	Flow rate m/sec x)
Titanium	4.5	8.4	0.041	10.400	34	44	40	>20
18-8 Stainless Steel	7.9	17	0.039	19.600	20	61	60	>20
Admiralty Brass	8.53	20.2	0.26	11.200	14	35	65	2
90-10 Cupro-nickel	8.94	17.1	0.11	12.600	14	36	42	4
70-30 Cupro-nickel	8.95	16.2	0.07	15.400	18	43	45	2-3
Aluminium Brass	8.33	18.5	0.24	11.200	18	46	55	2-3

x) Tolerable flow rate without erosion corrosion.

Table 5. Use of Titanium in Heat-Exchangers at Ekofisk /10/.

Exchanger Description	Tube Side	Shell Side
Discharge cooler	Hydrocarbons 136 atm.	Seawater
Propane condenser	Seawater	Hydrocarbons 68 atm.
Gas-dehydrator cooler	Seawater	Gas and hydro carbons 68 atm.
Interstage oil cooler	Seawater	Crude, low pressure
Flash gas compressor intercooler	Seawater	Flash gas and hydrocarbons 20 atm.
Glycol cooler	Seawater	Ethylene glycol, low pressure
Quench water-cooler	Seawater	Fresh water, low pressure

Table 6. Alloy Failure Mechanism in Tubes where Titanium has Behaved Satisfactory. Collection of Data from 64 Case Histories with Heat Exchangers in U.S. oil Refineries /6/.

Alloy	Failure Mechanism
Carbon steel	General Corrosion
70-30 CuNi	Denickelfication in cooling water
70-30 CuNi	Sulfidation on process side
70-30 CuNi	Sulfidation on process side
Monel	Sulfidation on process side
Admiralty brass	Dezincification in cooling water
Incaloy 800	Intergranular attack (nitric acid service
316 Stainless	Pitting
304 Stainless	Stress corrosion, intergranular cracking
Aluminium	Erosion

TABLE 7

FAILURE OF CONDENSER TUBING MATERIAL IN SEAWATER (R.I. JAFFEE) (PERCENT IN 10^4 HOURS)

	90-10 Cu-Ni	70-30 Cu-Ni	Al-Brass	Al-Bronze	Ti	Σ
General corrosion or unknown	4.6	0.7	1.7	16.0	0.0	23.0
Erosion-corrosion	5.9	1.5	7.4	16.0	0.0	30.8
Pitting	10.5	1.3	2.3	32.0	0.0	46.1
Vibration and mechanical damage	0.0	0.0	0.0	0.0	0.1	0.1
Σ	21.0	3.5	11.4	64.0	0.1	100.0

TABLE 8

PRICE COMPARISON OF SEVERAL SEAWATER RESISTANT MATERIALS

Alloy	Price NOK/kg[1]	Density kg/dm^3	Price kr/dm^3	Relative price compared to AISI 316
316 L	45- 50	7,9	355- 395	1
254 SMO	70- 80	8,0	560- 640	1,5 - 1,7
90/10 Cu-Ni	60- 70	8,9	534- 623	1,4 - 1,7
NiAl-bronse	60- 70	7,6	456- 532	1,2 - 1,4
Monel 400	70- 80	8,8	616- 704	1,6 - 1,9
Monel K-500	70- 80	8,8	616- 704	1,6 - 1,9
Inconel 625	170-240	8,4	1428-2016	3,8 - 5,4
Titanium (unalloyed)	150	4,5	675	1,8

[1]) Prices are taken from R. Johnsen. Ingeniør-nytt, 28/85 1985 /27/.

TABLE 9

PRICES ON SOME HEAT EXCHANGER TUBES 1984

Material	NOK/m
Monit	29
984 LN (254 SMO)	31
Titan grade 2	35

Tube OD 19 * wall thickness 0.7 mm
(OD 3/4" * 22 BWG)
Quantity: 100 000 m

TABLE 10

LIFE CYCLE COST OF A CONDENSOR. ALBRASS VS TITANIUM. SEAL WELDED IN A NUCLEAR POWER PLANT /20/

	Albrass	Titanium
Outage cost (0.4 M$/day)	12 M$	12 M$
Cost of tubes + retubing	3.5 M$	8.0 M$
Cost today of retubing	15.5 M$	20 M$
Capitalized cost, for future retubing	7.8 M$	-
Capitalized cost, leak and maintenance (Cost of one leak 50 000-100 000 $)	7 M$	
Difference in favour of Titanium		10.3 M$

These economical calculations have been performed with 12% interest and 1 US $ = 8 Sw.Cr. The size of the unit is 1000 MWe and the amount of tubes is 50 000.

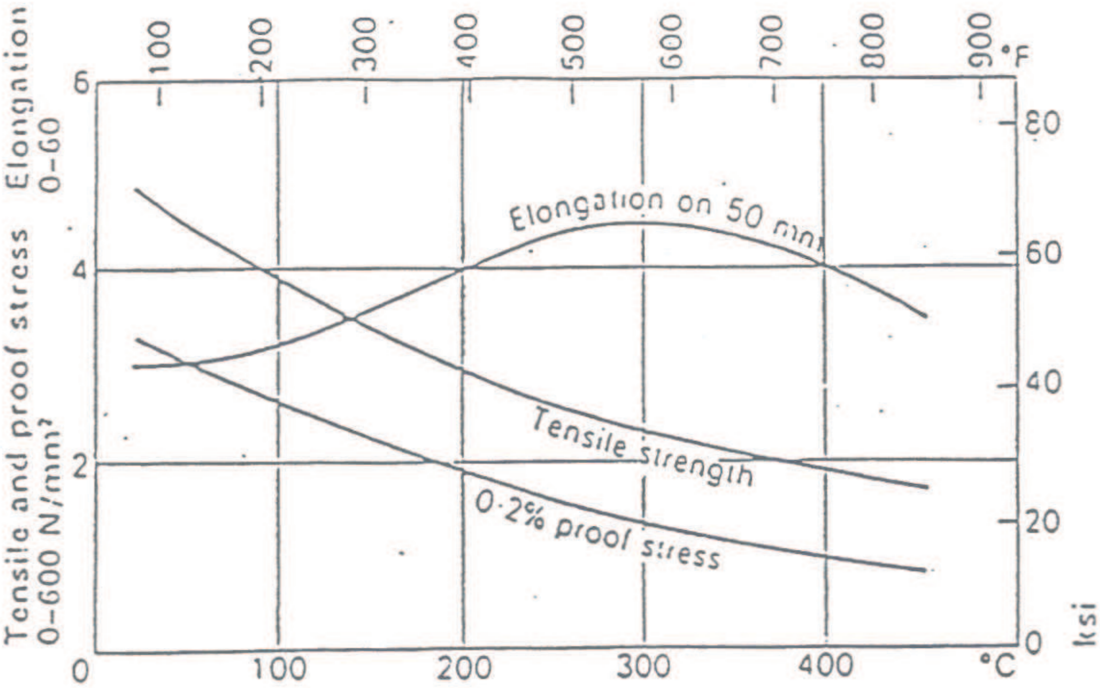


Figure 1   Grade 2 (IMI Titanium 125) - typical tensile properties /2/.

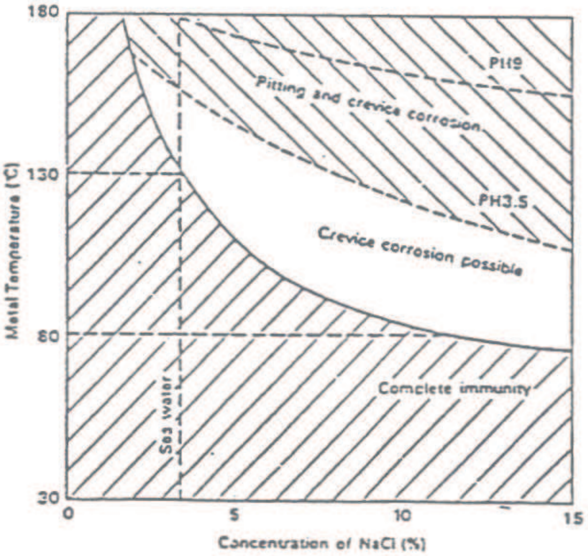


Fig. 2.   Influence of temperature, NaCl concentration and pH on crevice corrosion and pitting corrosion of commercial pure titanium /9/.

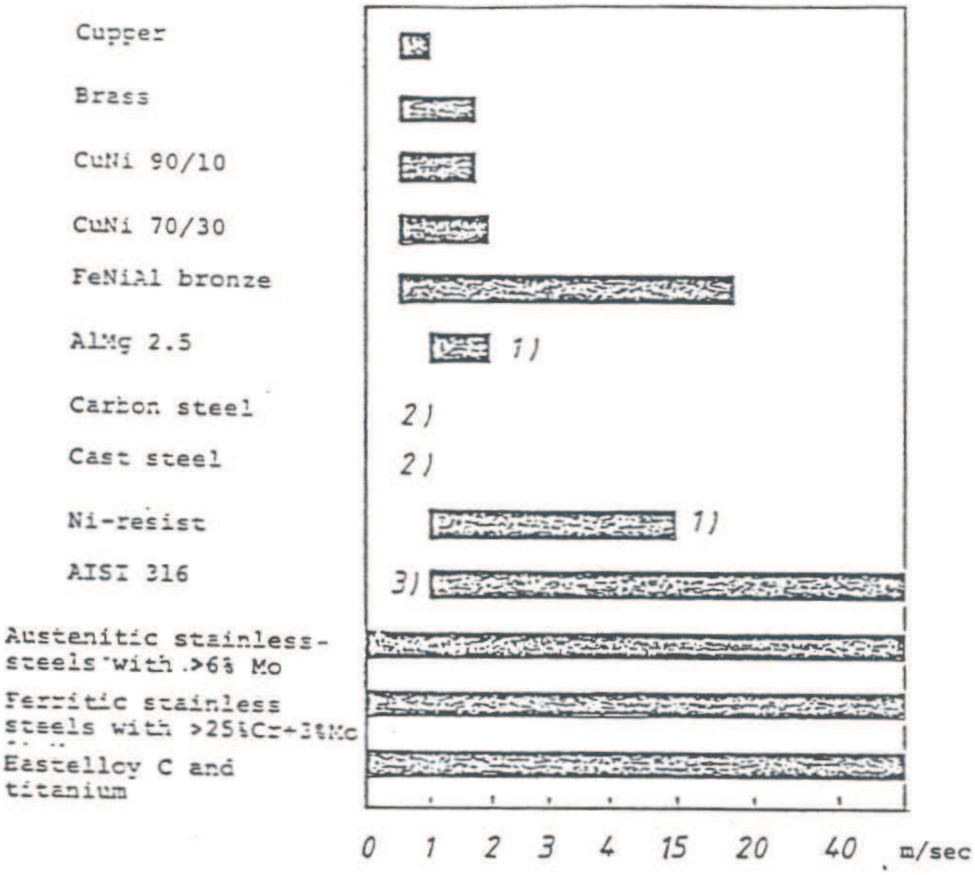


Fig. 3. Acceptable flow rate in seawater below 40°C. (Ref. 8)

1) Limited documentation.
2) Should not be used without protecting layer or cathodic protection.
3) Prone to crevice corrosion at unfavourable geometries.

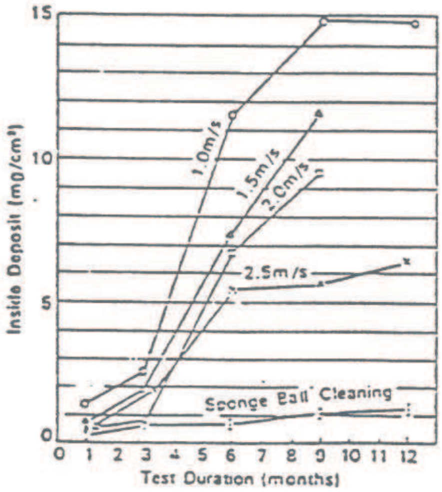


Fig. 4. Influence of the flow rate of seawater and sponge ball cleaning on the tendency to fouling in titanium tubes /10/.

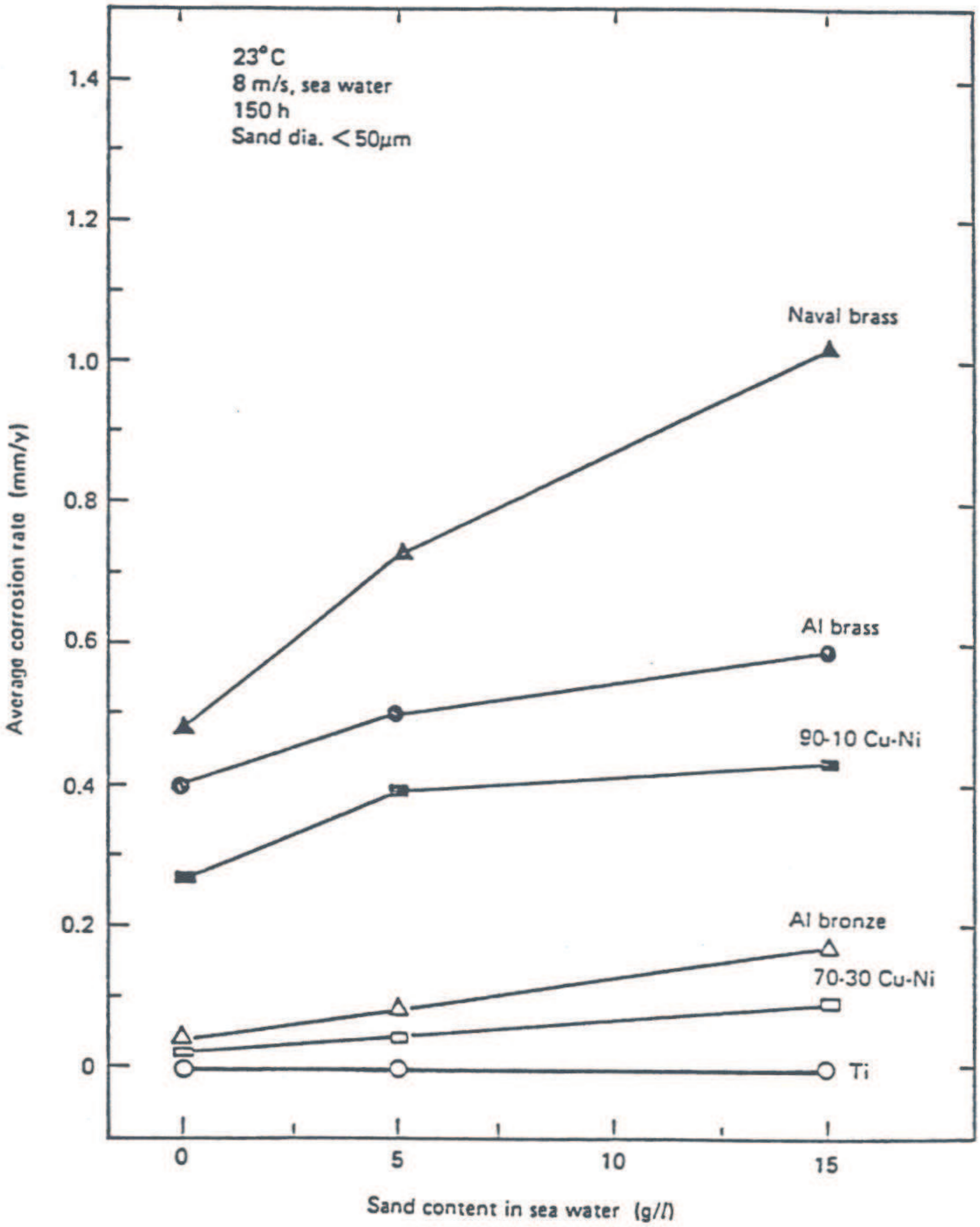


Fig. 5. Effect of sand content on corrosion rates of copper alloys and titanium in flowing sea water /1/.

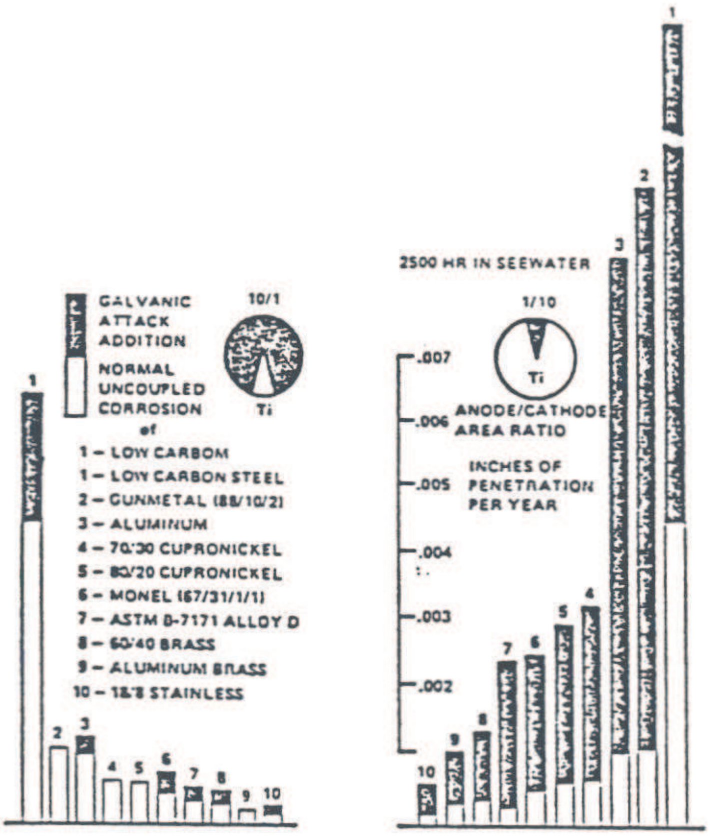


Fig. 6. A summary of the effect of dissimilar metal coupling on corrosion rates in seawater /9/.

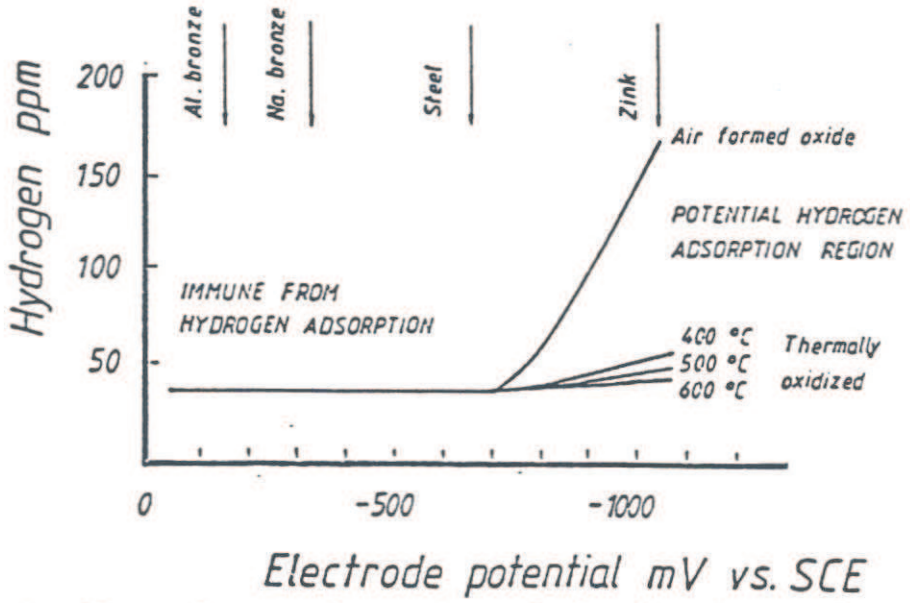


Fig. 7a. Hydrogen absorption of titanium in synthetic seawater at increasing cathodic potential /9/.

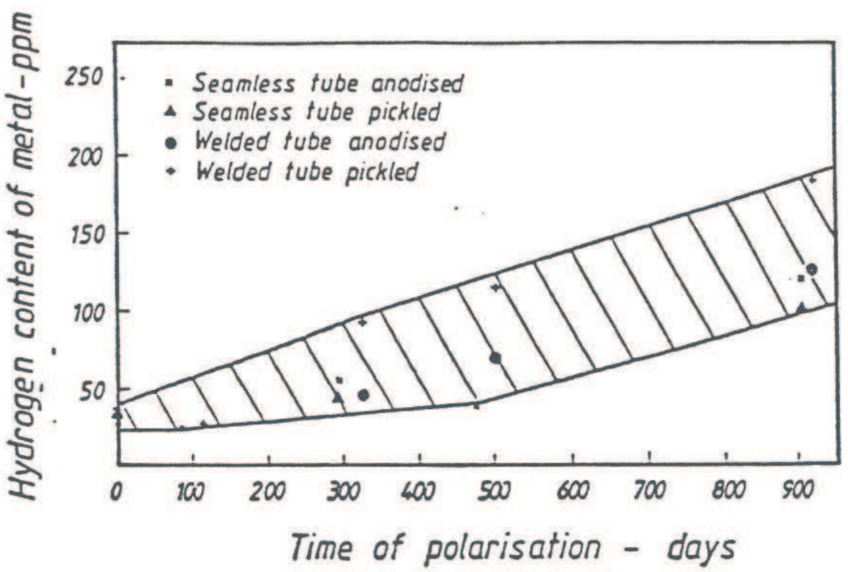


Fig. 7b. Hydrogen uptake by commercially pure titanium tube polarised cathodically in synthetic seawater, pH 8.9, at room temperature to -950mV SCE /12/.

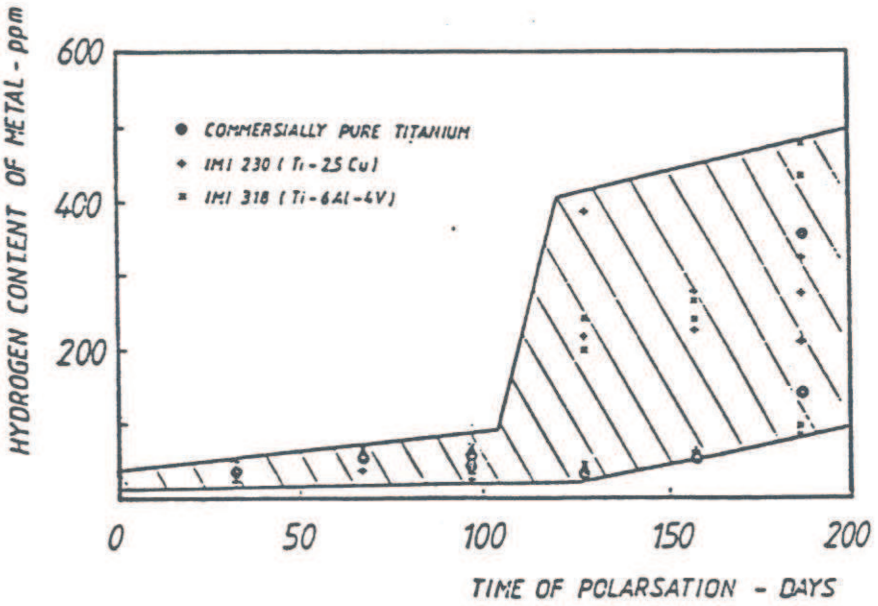


Fig. 7c. Hydrogen uptake by titanium sheet sampled polarised cathodically in synthetic seawater, pH 8.9, at 60°C to -950mV SCE /12/.

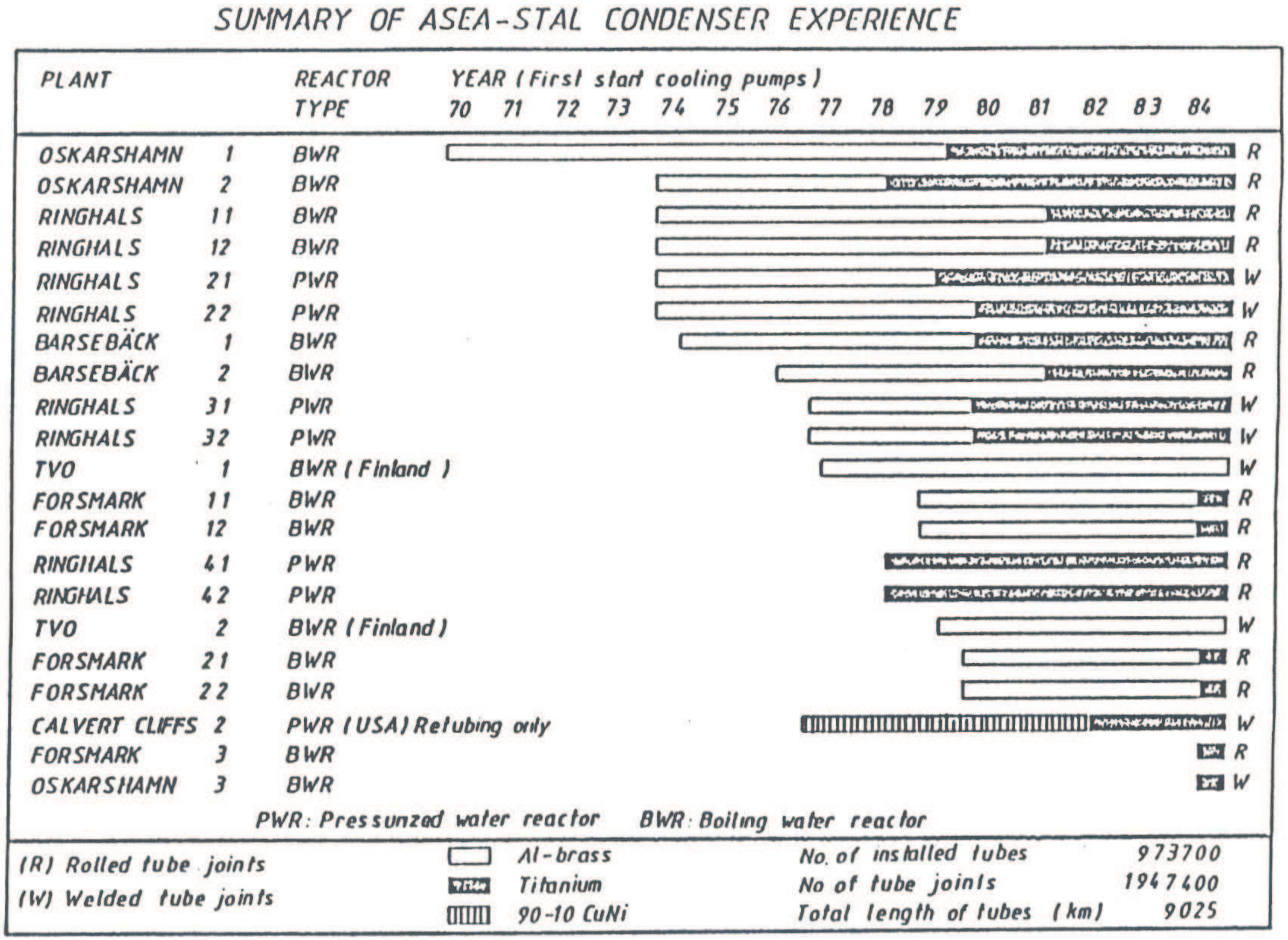


Fig. 8. Summary of ASEA-Stal condensor experience /20/.

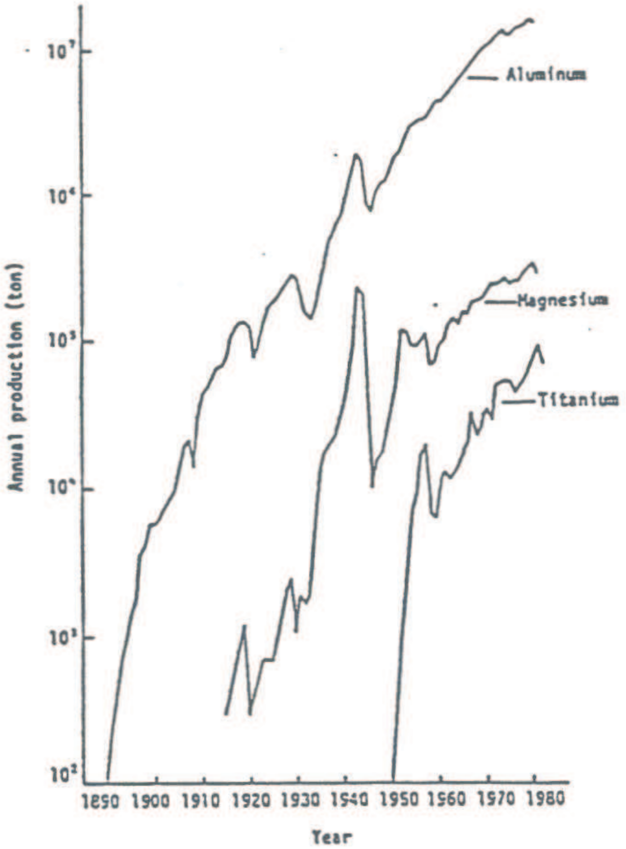


Fig. 9. World Production of Aluminum, Magnesium and Titanium /25/.

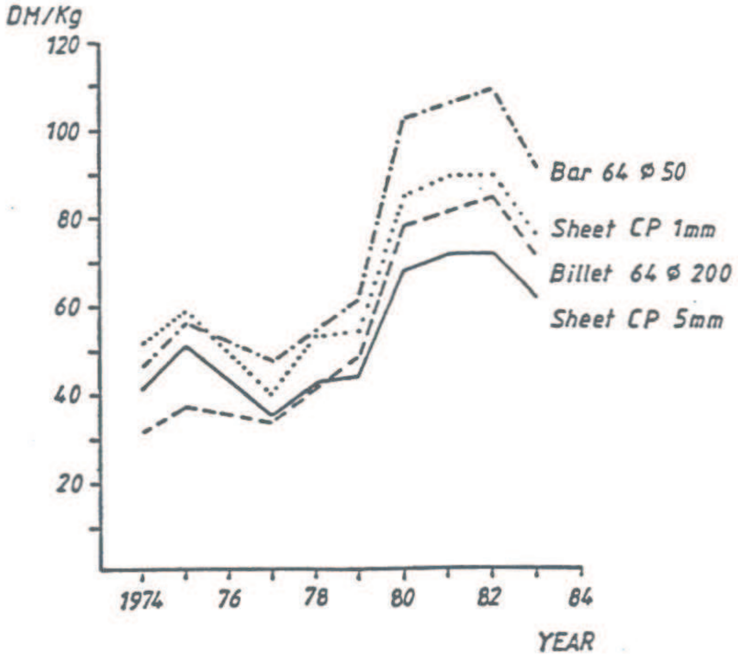


Fig. 10. Prices on mill products of titanium 1974-1983 /28/.

Max X. Cerny,
The Pfaudler Company - U.S.A.

APPLICATION OF TITANIUM LININGS IN FLUE GAS DESULFURIZATION SYSTEMS

1 - INTRODUCTION

Wet scrubbing of boiler flue gas is currently the primary method for successfully controlling sulfur dioxide emissions from coal-fired power plants. Past operational experience with these wet FGD scrubbers, however, has shown that highly corrosive conditions often develop in inlet quench, absorber, outlet, and stack zones of these systems. These aggressive zones are generally the result of wet/dry interfaces, hot oxidizing, acidic condensates, and flyash-laden duct wall deposits which are enriched in chloride and fluoride species. These conditions have contributed to numerous cases of accelerated localized corrosion failure of steel, stainless steels, and nickel alloy linings and various steel coatings reported in these systems. (1-5)

Based on extensive field (6-9) and laboratory (10-11) corrosion testing since 1981, titanium has become qualified as a prime corrosion-resistant material for inlet quench, outlet duct, and stack linings of wet FGD scrubbers. The in situ test exposures, along with service experience from a number of full-size power plant scrubber lining installations in the U.S., have confirmed titanium’s superior performance despite wide variations in scrubber chloride levels and other operating parameters. Other attributes of titanium as a durable and practical liner material include its favourable strength and ductility, excellent abrasion resistance, relatively low density (light-weight) and coefficient of expansion (reduced thermal stresses), and its reasonable shop and field fabricability and weldability.

Furthermore, it is readily available in mill-quantity sheet and strip forms, and has an attractive cost (on a per unit surface area basis) which falls between the common stainless steels and high nickel alloys.

Despite all of these favourable attributes, experience has shown that cost effective application of titanium linings in FGD systems is highly dependent on installation methodology. This paper compares the current methods for installing liners, and identifies the most practical method via cost analysis. Details on titanium liner installation and quality assurance are reviewed along with several examples of full-size power plant lining installations in the U.S.

2 - TITANIUM LINING METHODS

Titanium sheet linings are applied to FGD systems via three commercially-available and proven methodologies:

1) Fastened-on loose sheet lining,
2) Titanium explosion-clad steel plate construction,
3) Resista-Clad Plate lining and construction.

2.1 - Fastened-On-Sheet

The traditional method for lining steel ducting or vessels with thin (1.5-2 mm thick) titanium sheets involves fastener attachment (12). Fastening is achieved by titanium or steel bolts (typically 6.3 or 9.5 mm dia.) threaded into the drilled and tapped steel substrate wall, or fastened with a nut from the steel backside surface when accessible; or by a threaded steel stud resistance-welded to the steel wall surface onto which a steel nut is fastened. Aligned holes in the titanium sheet facilitate sheet attachment with these fasteners. A metal seal at fastener sites is achieved by circumferentially filet-welding titanium bolt heads to the sheet, or filet-welding a small titanium sheet cap or cover over the steel fastener sites. Filet-welding of overlapping adjoining titanium sheets permits a total liner seal.

Although applicable for either retrofit lining or new construction, this method is very labour intensive and time consuming due to the drilling, tapping and extra seal welding required at fastened sites. As a result, mechanically-fastened titanium linings have been found to be approximately 30-40% more costly than nickel alloy "wallpapers" which are plug-welded to steel walls.

2.2 - Explosions-Clad Construction

Titanium sheets down to 2 mm can be 100% pre-bonded to a thick (≥ 9.5 mm) steel backer plate via explosive welding. However, due to its relatively thick steel backer, this product is more practical for new duct or vessel construction rather than retrofit linings. Standard fabrication methods involve butt-welding steel backer plates together, followed by filet-welding a titanium sheet batten strip over the welded plate joint. Since rather thin (typically 6-8 mm) duct walls are involved in FGD systems, the relatively high cost of titanium explosion-clad plate (about USD $100/ft^2$ or USD $1080/m^2$) results in an installed cost approximately 20% higher than fastened sheet liner methods.

2.3 - Resista-Clad Plate

Titanium sheet of virtually any thickness which is selectively pre-bonded to any thickness steel plate or sheet is commercially available as Resista-Clad Plate (13).

This patented resistance-braze seam process produces 6.3mm wide bond seams, exhibiting typical shear and peel strength values of 44 ksi (303 MPa) and 835 lb/in (15 kg/mm), respectively, which can be spaced or locally pre-applied per service requirements (14). Due to the flexibility in plate sizes (up to 12 ft (3.7m) wide x unlimited length) and thicknesses available, this clad product is applicable for retrofit linings (typically 1.6 mm Ti/1.6 mm steel) as well as new duct and vessel construction (typically 1.6 mm Ti/6-9 mm steel). Furthermore, Resista-Clad Plate can be manufactured with the titanium sheet offset in two directions from the steel backer to facilitate retrofit lining installation via overlap of adjoining plates (similar to roof "shingling", see Fig. 1). Similarly, the titanium sheet can be recessed from the steel backer on all sides to facilitate steel backer butt-welding and titanium batten strip seal welding in new construction (Fig. 2) .

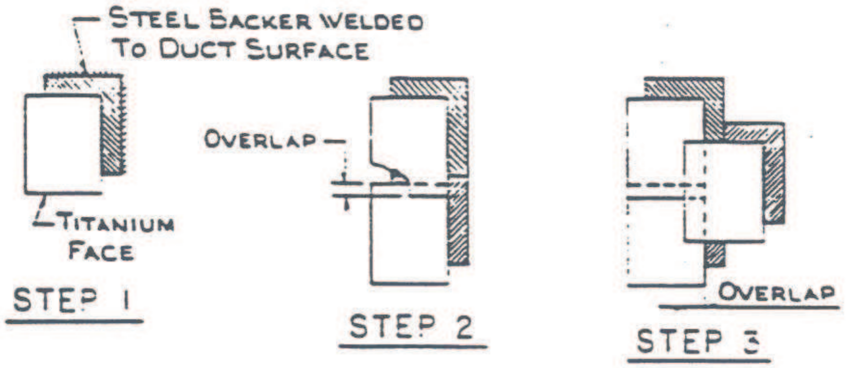


Fig. 1 - Typical pattern of steel wall attachment and overlap of titanium Resista-Clad Plates for retrofit linings.

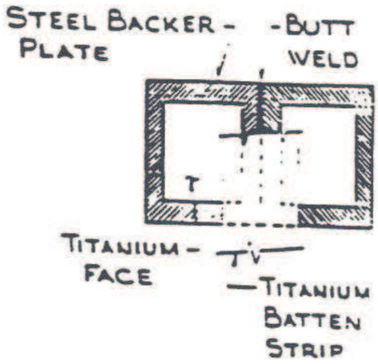


Fig. 2 - Typical titanium Resista-Clad Plate construction for new or total duct/vessel wall construction

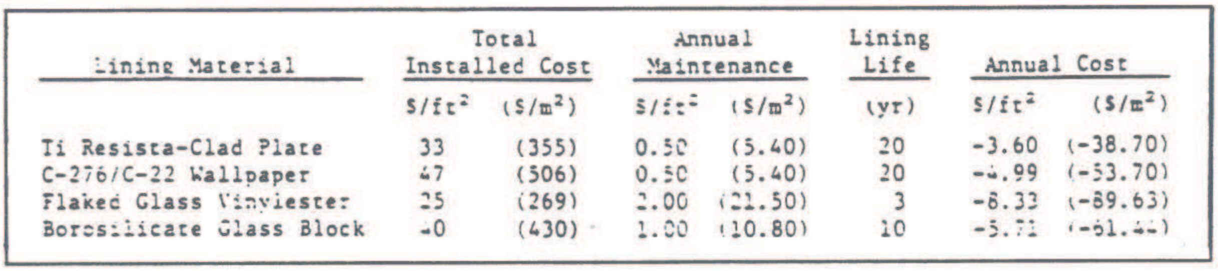
The virtue of pre-bonding titanium to steel precludes the need for costly mechanical fastening while minimizing seal welding. For retrofit lining, plate to wall attachment is reduced to simple and inexpensive steel plate backer-to-steel wall filet welding. After Resista-Clad Plate attachment, a total retrofit liner seal is achieved by filet-welding of overlapping plates. These labor and time saving benefits afforded by the relatively inexpensive seam bonding process results in an installed cost of Resista-Clad Plate ~50% and 60% that of explosion-clad and fastened-on titanium liners, respectively, in new construction; and ~50% that of fastened-on sheet liners in retrofit lining jobs. Titanium Resista-Clad Plate retrofit installation costs are approximately 25-30% below those of nickel alloy wallpapers, while circumventing the cost and reliability problems associated with nickel alloy "wallpaper" plug-welding.

2.4 - Conclusion From Comparison of Available Methodologies

It can be concluded from the prior overview of current cornrnercially-available titanium lining methods that the Resista-Clad Plate approach has significant installed cost advantages over other lining options, while practical and reliable in actual field installations. Therefore, the balance of this paper will limit its scope to aspects of Ti Resista-Clad Plate linings for utility FGD systems.

3 - EFFECTIVE ANNUAL COST COMPARISON FOR FGD LININGS

A discounted cash flow (or net present value) analysis was conducted to calculate the effective annual cost of various FGD retrofit lining options. The assumptions for initial installed cost, annual maintenance, and lining life are outlined in Table 1 for each lining type. Rate of return was assumed to be 10% and an effective tax rate of 36%. Despite the conservative life assumed for titanium, the Ti Resista-Clad Plate lining is most attractive economically (Table 1).



Lining Material	Total Installed Cost		Annual Maintenance		Lining Life	Annual Cost	
	\$/ft²	(\$/m²)	\$/ft²	(\$/m²)	(yr)	\$/ft²	(\$/m²)
Ti Resista-Clad Plate	33	(355)	0.50	(5.40)	20	-3.60	(-38.70)
C-276/C-22 Wallpaper	47	(506)	0.50	(5.40)	20	-4.99	(-53.70)
Flaked Glass Vinylester	25	(269)	2.00	(21.50)	3	-8.33	(-89.63)
Borosilicate Glass Block	40	(430)	1.00	(10.80)	10	-5.71	(-61.44)

Table 1: Discounted cash flow analysis of various FGD system lining options

4 - FGD SYSTEMS LINING REQUIREMENTS

In addition to resisting the harsh chemical environment, FGD wet scrubber system linings must accommodate various design and operating stresses. These include internal gas pressure, thermally-induced stresses (370°C max. temperature), shear and/or tensile gravity-induced (hanging) stresses, physical impact or bending from duct maintenance activities, and various forms of vibratory stresses induced from flue gas flow, rotating equipment, and external blowing winds. With the exception of internal gas pressure and physical abuse, all other stresses listed are calculated to be on the order of a few ksi or less (<15 MPa) and are, thus, generally not limiting for Resista-plate liners. A good metal liner fit-up to within 1.3cm of the duct surface will minimize bending and physical damage.

Based on typical FGD duct pressures ranging from -13 to +25 cm H_2O and -25 to +50 cm H_2O during upsets, negative internal duct pressure is often the most critical design parameter in these systems.

Designing with a safety factor of 3, the combined stress on Resista-Clad plate is maintained below 15 ksi (103 MPa) under upset condition negative pressures by a maximum bond seam spacing of 12-18 in (30-46 cm) and a maximum plate width of 4 ft (1.2m). For retrofit installations, clad steel plate to steel duct filet welds on two sides of each plate should also be continuous or no less than a 8 cm long on 15 cm center stitch (Fig. 1).

5 - LINING INSTALLATION PROCEDURES

Figures 1 and 2 schematically depict how Resista-Clad Plates are installed as retrofit linings and for new construction, respectively. The retrofit method is best described as a "shingling" process in which the lining is applied at an approximate rate of 3000 ft^2/wk (280 m^2/wk) in FGD ducting. On the other hand, the new construction method is similar to the batten strip weld joint procedure commonly utilized in explosion-clad construction.

The basic steps for applying retrofit Resista-Clad lining include:

1) Remove existing duct, stack, or absorber wall coating(s).

2) Thoroughly clean steel substrate surface with a commercial blast (SSPC-SP6) or white metal blast (SSPC-SP5).

3) Per Figure 1 pattern, tack up two sides of each Resista-Clad Plate (steel backer) onto cleaned steel surface using coated stick carbon steel electrodes. If possible, attach plates from top to bottom on horizontal Walls.

4) Apply continuous or stitch (8 cm long on 15 cm centers) carbon steel weld seams along the two tacked up sides of each plate backer using coated stick electrodes. E-7018 electrodes are preferred for white metal blast surfaces for strength reasons. E-60XX electrodes with continuous weld seams are suitable for commercial blast surfaces.

5) Clean dirt, debris, grease, and oxide films off of titanium sheet surfaces ~4 cm around seam weld joint via stainless steel wire brushing to silver metal, followed by a clean acetone wipe just prior to welding.

6) Achieve good overlapping titanium sheet fit-up (<1.5mm) using fit-up or cheater bars, and spot weld (tack) titanium seams via hand-fed TIG at 2.5-5.0 cm intervals.

7) Using hand-fed wire TIG, spot weld prefabricated and performed titanium sheet joint covers, corner pieces, transition pieces, or flanges into place onto titanium sheet surfaces.

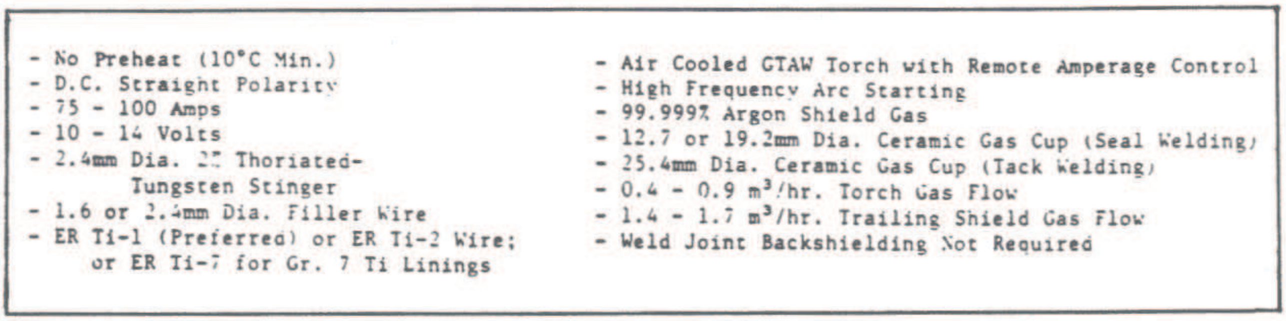
8) Remove lightly oxidized spot weld surfaces by stainless steel wire brushing and reclean joints with acetone wipe. Grind out any heavily contaminated spot welds, clean up joint surface, acetone wipe clean, and reweld.

9) Filet weld all overlapping titanium sheet joints via hand-fed wire TIG to achieve a total lining seal.

10) Final inspection of titanium weld seams.

6 - WELDING REQUIREMENTS

Basic parameters for hand-fed wire GTA (TIG) welding of titanium sheet overlap seams are presented in Table 2. Quality titanium seam welds require totally clean and oxide-free joint surfaces, and complete face and trailing inert gas shielding as indicated. To limit air contamination both gas shields should be purged prior to welding, and weldments post-purged with argon 30 seconds or until metal temperatures tall below 370°C. Aluminium foil skirts attached to trailing shields further minimize contamination from air drafts. Drafts should be stifled by isolating work areas using dampers or temporary barriers. Titanium filler wire surfaces must be clean and air-contaminated ends cut off. High frequency arc starting and sharp tungsten stingers help minimize localized weld defects as well.



- No Preheat (10°C Min.)
- D.C. Straight Polarity
- 75 - 100 Amps
- 10 - 14 Volts
- 2.4mm Dia. 2% Thoriated-
  Tungsten Stinger
- 1.6 or 2.4mm Dia. Filler Wire
- ER Ti-1 (Preferred) or ER Ti-2 Wire;
  or ER Ti-7 for Gr. 7 Ti Linings

- Air Cooled GTAW Torch with Remote Amperage Control
- High Frequency Arc Starting
- 99.999% Argon Shield Gas
- 12.7 or 19.2mm Dia. Ceramic Gas Cup (Seal Welding)
- 25.4mm Dia. Ceramic Gas Cup (Tack Welding)
- 0.4 - 0.9 m^3/hr. Torch Gas Flow
- 1.4 - 1.7 m^3/hr. Trailing Shield Gas Flow
- Weld Joint Backshielding Not Required

Table 2: Details for GTA filet-welding of 1.6mm titanium sheet overlap seams in field installations.

Using these parameters, a titanium seam weld rate of 2-5 in/min (5-13 cm/min) can be anticipated depending on joint fit-up and position. An estimated total welding rate which includes surface preparation, tack welding. and seam weld-out is 10 ft/hr (3 m/hr). Lining bowing and distortion can be minimized by tack and seal welding the top and bottom (or opposing sides) of titanium plates simultaneously to balance weld-induced stresses.

Assessment of titanium tack or seam weld quality in the field is achieved through four basic methods: close visual inspection, weld surface colour, tungsten scratch testing, and liquid dye penetrant inspection. Silver, straw, gold or light blue coloured single-pass welds are generally considered to be acceptable.

However, dark-blue, iridescent, gray or white coloured titanium weldments are probably heavily contaminated and must be rejected. If local weld areas are of questionable quality relative to colour, tungsten rod scratching to compare the relative hardness of weld surfaces to adjacent base metal may further discern quality. If the weld does not scratch easily or at all compared to base metal, poor weld quality is indicated. Close visual inspection and final dye penetrant inspection are useful for detecting gross weld defects, voids, and cracks. Any titanium welds not meeting the prior quality tests must be ground-out and rewelded after the joint has been re-cleaned and wiped with acetone.

Welders should be qualified in GTA-welding titanium in accordance with ASME Pressure Vessel Code Section IX guidelines. Qualification criteria can include weld colour, tungsten scratch hardness, and sample weld joint bend tests. The longitudinal weld bend sample should pass a 5T bend radius criteria when the filet-weld face is on the bend O.D. surface.

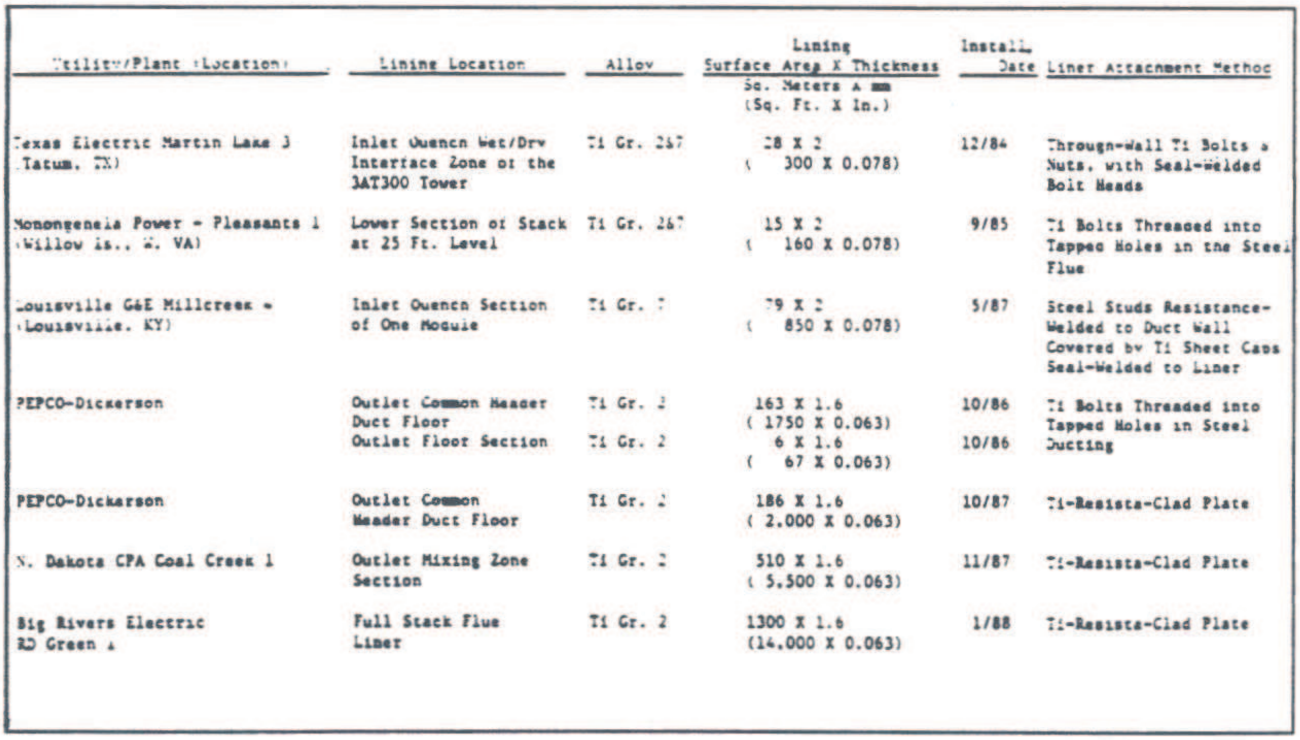
7 - TITANIUM LINING INTERFACES

Installation of titanium linings in FGD systems often requires a transition of the lining to other components or dissimilar linings. Although titanium cannot be successfully welded to ferrous or nickel alloys, several practical options are available. These methods involve mechanical seals, organic coating or sealant overlap, and total metal seals. Mechanical seal strategies include prefabricated integral titanium sheet flanges sealed into gasketed expansion joints (preferred whenever possible), or thin titanium plate strip flanges fastened down at the titanium lining periphery and incorporating an elastometric gasket (e. g. Viton) or sealant to effect a seal. Effective organic coating or sealant overlap transitions from coated steel surfaces require proper titanium surface preparation for maximum coating adherence. This is achieved by local sandblasting and subsequent cleaning of peripheral titanium surfaces to be coated prior to coating application.

Explosion-clad transition strips and Resista-Clad bond seams both provide total metal seals for titanium lining to duct/vessel wall interfaces. Either option offers wide flexibility in titanium to dissimilar metal transition combinations available, so that transition strips of titanium to steel, stainless steel, or nickel alloys can be used. Transition strip widths on the order of 8 cm permit titanium to titanium lining seal welds and dissimilar metal to duct wall filet-welds to be made. The Resista-Clad transitions are generally more cost-effective and can readily bond titanium sheet to nickel alloy (i.e. 625 or C-276) sheet for more corrosion-resistant peripheral seals.

8 - UTILITY FGD INSTALLATIONS

Table 3 describes installed full-size titanium linings currently in service in U.S. utility wet FGD systems. Corrosion-and trouble-free performance of these linings have been reported to date.



Utility/Plant (Location)	Lining Location	Alloy	Lining Surface Area X Thickness Sq. Meters X mm (Sq. Ft. X In.)	Install. Date	Liner Attachment Method
Texas Electric Martin Lake 3 (Tatum, TX)	Inlet Quench Wet/Dry Interface Zone of the 3AT300 Tower	Ti Gr. 2&7	28 X 2 (300 X 0.078)	12/84	Through-Wall Ti Bolts & Nuts, with Seal-Welded Bolt Heads
Monongehela Power - Pleasants 1 (Willow Is., W. VA)	Lower Section of Stack at 25 Ft. Level	Ti Gr. 2&7	15 X 2 (160 X 0.078)	9/85	Ti Bolts Threaded into Tapped Holes in the Steel Flue
Louisville G&E Millcreek - (Louisville, KY)	Inlet Quench Section of One Module	Ti Gr. 7	79 X 2 (850 X 0.078)	5/87	Steel Studs Resistance-Welded to Duct Wall Covered by Ti Sheet Caps Seal-Welded to Liner
PEPCO-Dickerson	Outlet Common Header Duct Floor Outlet Floor Section	Ti Gr. 2 Ti Gr. 2	163 X 1.6 (1750 X 0.063) 6 X 1.6 (67 X 0.063)	10/86 10/86	Ti Bolts Threaded into Tapped Holes in Steel Ducting
PEPCO-Dickerson	Outlet Common Header Duct Floor	Ti Gr. 2	186 X 1.6 (2.000 X 0.063)	10/87	Ti-Resista-Clad Plate
N. Dakota CPA Coal Creek 1	Outlet Mixing Zone Section	Ti Gr. 2	510 X 1.6 (5.500 X 0.063)	11/87	Ti-Resista-Clad Plate
Big Rivers Electric RD Green 1	Full Stack Flue Liner	Ti Gr. 2	1300 X 1.6 (14.000 X 0.063)	1/88	Ti-Resista-Clad Plate

Table 3: Full-size titanium lining installations in utility FGD systems.

9 - SUMMARY

A review of commercially-available titanium lining methodologies for utility FGD systems indicate that titanium Resista-Clad Plate offers significant economic and practical advantages for both retrofit and new construction of lined FGD systems. Since titanium sheet is pre-bonded to steel plates by this method, the high cost of mechanical fastening, related seal welding, and the plug-welding of nickel alloy "wallpapers" is circumvented. As a result, titanium Resista-Clad Plate offers initial installed cost and/or life cycle cost advantages over many other FGD lining materials. Procedures for field welding, installation, and quality assurance of titanium Resista-Clad Plate linings have been established and are outlined in the paper. Examples of successful FGD system lining applications in U.S. power plants are cited as well.

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CONTINUOUS CASTING OF TITANIUM IN COLD CRUCIBLE

SYNOPSIS

The C.C.C.C. (cold crucible continuous casting) is a new process for the induction melting and casting of high melting point reactive materials. Continuous billet extraction can be carried out without the need for a slag, provided that the design is optimized and that the frequency and the transmitted power are adapted to suit the material to be melted.

The CEZUS plant enables the production of 150 mm diameter and several meters length billets. By melting titanium turnings, sound billets are obtained with a good surface quality, a fine solidification structure and a good control of the chemistry.

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1 - INTRODUCTION

Titanium, which melts at 1660°C, has a marked affinity for oxygen and carbon. So induction melting is a process which is difficult to apply to titanium, since reaction between the liquid metal and the refractory crucible lining (oxyde ceramic or graphite) leads to pollution of the titanium.

For several years, CEZUS, in collaboration with the CNRS MADYLAM laboratory has experimented with a new type of induction furnace which allows the clean melting of titanium. The main feature of this furnace is the crucible which is a cooled copper crucible, made up of a number of separate segments to promote electromagnetic coupling with the metallic charge.

This new process called C.C.C.C. (cold crucible continuous casting) (1) involves:

- continuous melting of the divided charge material or a consumable electrode.
- solidification of the liquid metal.
- continuous extraction of the solidified billet.

The system is designed to operate without slag, a significant improvement compared to the "Inductoslag ingot melting" process, developed in the past by the U.S. Bureau of Mines (2).

It avoids numerous difficulties such as slag supply to the crucible, volatilisation, furnace cleaning constraints, billet peeling requirements, etc ...

Another point is that device allows to reach very high temperatures and not only titanium but also zirconium, niobium and even molybdenum have been successfully melted.

2 - EXPERIMENTAL INSTALLATION

The CEZUS plant shown schematically in figure 1 comprises:

- a cooled double-walled stainless vessel,
- a charging system consisting of a stainless steel hopper, vibrators and a chute,
- a water-cooled segmented copper crucible,
- a cooled inductor,
- a mechanical billet extraction system.

The inductor is supplied by a medium frequency static generator. A pump unit enables a vacuum to be established in the furnace, and if required, it is possible to introduce an inert gas.

3 - MELTING OF TITANIUM TURNINGS

The cold crucible induction furnace has been used to melt titanium and titanium alloy turnings. The melting procedure is as follows.

- The hopper is filled with turnings.
- A titanium primer with a diameter slightly smaller than that of the crucible is installed to contain the initial liquid.
- The furnace and hopper are pumped down to 10^{-2} torr and then filled with argon.
- The operating frequency is set by selecting the value of the adjustment capacitor in accordance with the inductor characteristics.
- When the impedance has been adapted, the power is gradually transmitted to the charge until it melts, with

the formation of a dome. The power is then adjusted to maintain a fluid bath and to control the height of the dome.

- The supply of turnings and the simultaneous continuous extraction of the billet can then be started.
- Melting is stopped when the desired length of billet is attained.

4 - OPERATING PARAMETERS

It is important that a suitable operating frequency be selected for the melting process to proceed in a satisfactory manner. In fact, the choice depends on the effects required, since there are three coexisting frequency dependent phenomena:

- a thermal effect (maximum energy dissipation in the charge),
- a pressure effect, which determines the form of the free surface of the liquid metal,
- a stirring effect in the metal bath.

Each of these phenomena can be favoured at the expense of the others by adjusting the frequency. An optimum frequency can be shown to exist for each of the effects, and the three values are quite distinct.

The effect of frequency f is described by the dimensionless "screen parameter" $R\Omega$

$$R\Omega = \mu_o \sigma \Omega R^2$$

where: μ_o is the magnetic permeability of vacuum,
σ is the electrical conductivity of the material

at the melting temperature,
Ω is the frequency of the current in the inductor ($= 2\prod f$),
and R is the radius of the crucible.

$R\Omega$ can be shown to have the following characteristic values:

- 2: establishment of a plane free surface
- 25: optimum value for heating
- 40: optimum value for stirring.

The power transmitted is a second important parameter. It should be sufficient to melt the turnings, but must not produce too high a dome. In effect, it can be shown theoretically, and has been experimentally verified, that the dome height H is proportional to the magnetic field, and therefore to the power transmitted, through the relation:

$$H = B^2/2\mu_o lg$$

where:
B is the magnetic field strength inside the crucible,
l is the density of the liquid metal,
g is the acceleration due to gravity.

5 - RESULTS

Billets of excellent surface quality are obtained when the frequency and transmitted power are optimised and stable with time. Figure 2 shows a 100 mm diameter billet obtained from TA6V turningsj the skin is smooth and crack-free. On the contrary, the cracked surface of a billet of the same alloy shown in figure 3 illustrates the effect of a poor choice of frequency.

Table 1 compares the chemical analysis obtained on TA6V billet with that of the initial turnings.

	Al (%)	V (%)	Fe (ppm)	Cu (ppm)	O (ppm)	N (ppm)	C (ppm)
Turnings	6.2	4.1	1500	<50	2200	130	250
Billet	6.2	4.0	1550	<50	2250	120	260

It can be seen that there is no increase in the oxygen and nitrogen contents, nor in that of copper, showing that the crucible has not been attacked. Furthermore, melting under argon prevents the loss of volatile elements such as aluminium.

As in any induction melting process, stirring is extremely vigorous, In consequence, in spite of the steep thermal gradients induced by the use of a cold crucible, fine equiaxed macrostructures can be obtained in alloys such as TA6V. In general, the solidification structures produced by this process are found to be much finer than those obtained with the conventional consumable electrode arc melting technique.

6 - CONCLUSIONS

The C.C.C.C. (cold crucible continuous casting) is a new process for the induction melting of high melting point reactive materials. Continuous billet extraction can be carried out without the need for a slag, provided that the design is optimized and that the frequency and the transmitted power are adapted to suit the material to be melted.

By melting turnings, it has been shown in the case of titanium and its alloys that sound billets can be obtained with a good surface quality, a fine solidification structure and a good control of the chemistry.

The CEZUS plant enables the production of 150 mm diameter and several meters length billets suitable for direct extrusion or rolling.

7 - ACKNOWLEDGMENTS:

The authors wish to thank the AFME for partial support of this investigation.

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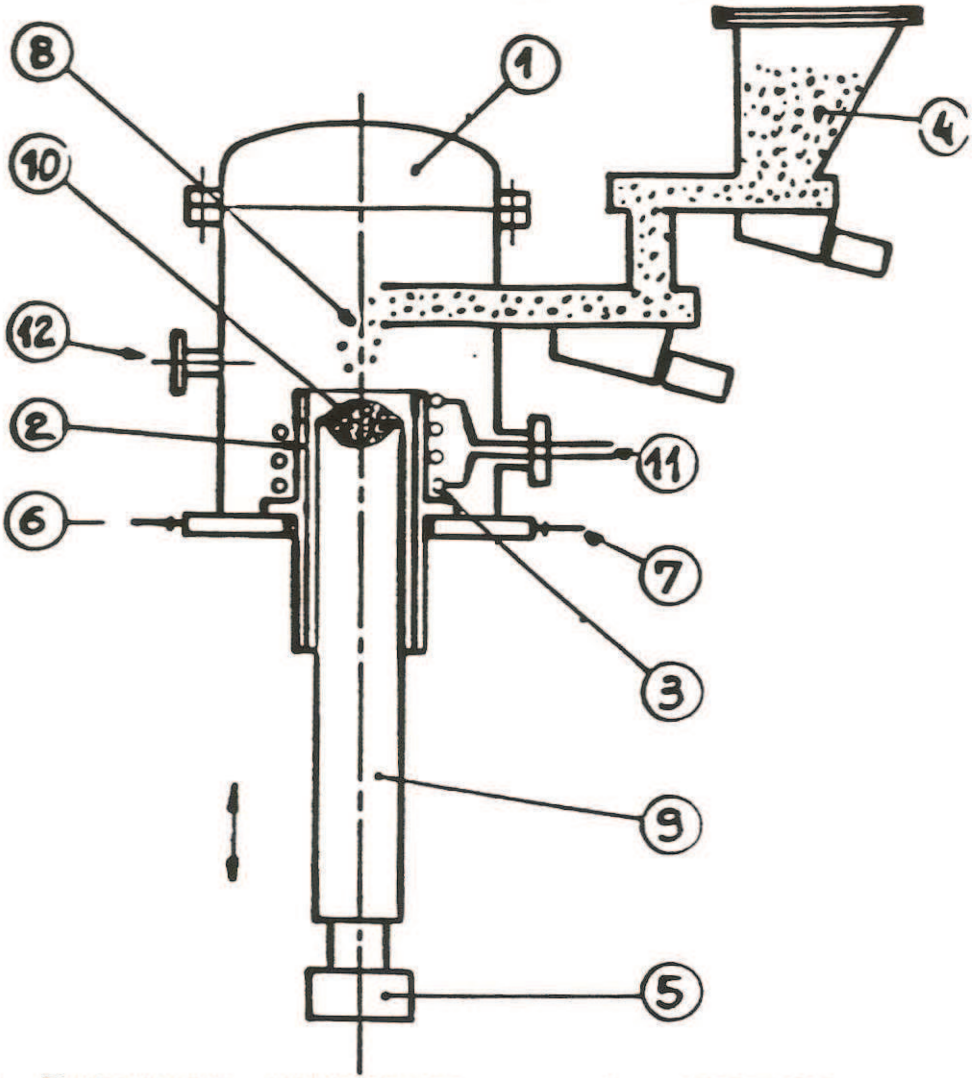
FIGURE 1

INDUCTION MELTING FURNACE



1_ FURNACE CHAMBER
2_ SEGMENTED CRUCIBLE
3_ COIL
4_ VIBRATING FEEDER
5_ INGOT WITHDRAWAL MECHANISM
6_ WATER INLET
7_ WATER OULET
8_ SCRAP
9_ INGOT
10_ POOL
11_ POWER CONNECTION
12_ TO VACUUM PUMP AND ARGON INLET

Figure 2

TA6V BILLET OBTAINED WITH THE C.C.C.C. PROCESS

Figure 3

CRACKED TA6V BILLET DUE TO A POOR CHOICE OF FREQUENCY

CONTINUOUS CASTING
OF TITANIUM
IN COLD CRUCIBLE

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CONTENTS

. DESCRIPTION OF A NEW PILOT PLANT CALLED C.C.C.C (COLD CRUCIBLE CONTINUOUS CASTING)

OPERATION AND EXPERIENCE ON TITANIUM MELTING

INDUCTION MELTING
OF REFRACTORY AND
REACTIVE METALS

PROBLEM

CONVENTIONNAL INDUCTION MELTING IN REFRACTORY CRUCIBLE ===> THE MOLTEN METAL REACTS WITH THE CRUCIBLE AND IS CONTAMINATED.

IT IS THE CASE OF TITANIUM

SOLUTION

INDUCTION MELTING IN COLD CRUCIBLE

EARLY EXPERIMENTS :

US BUREAU OF MINES

" INDUCTOSLAG INGOT MELTING "
" INDUCTOSLAG CASTING "

WITH CAF_2 SLAG

COLD CRUCIBLE

CONTINUOUS CASTING

CEZUS AND MADYLAM HAVE DEVELOPPED AND PATENTED A NEW DESIGN CALLED C.C.C.C ALLOWING :

- THE CONTINUOUS MELTING OF RAW MATERIAL OR CONSUMMABLE ELECTRODE
- THE SOLIDIFICATION OF METAL
- THE CONTINUOUS WITH_DRAWING OF THE SOLIDIFIED BILLET.

WITHOUT SLAG

HIGH TEMPERATURES

DESCRIPTION
OF THE PILOT
PLANT

DIFFERENT PARTS

- FURNACE
- MECHANICAL PUMP + INERT GAS CIRCUIT
- COOLING CIRCUIT
- MEDIUM FREQUENCY STATIC GENERATOR 200 KW + CAPACITORS
- INFORMATIC SYSTEM FOR FURNACE CONTROL

FURNACE

- VERTICAL WATER COOLED CHAMBER
- FEEDING SYSTEM WITH A HOOPER AND VIBRATORS
- SEGMENTED, WATER COOLED, COPPER CRUCIBLE
- WATER COOLED INDUCTION COIL
- BILLET WITHDRAWAL MECHANISM

===> BILLET DIAMETER : 150 MM
LENGTH : SEVERAL METERS

MELTING OPERATION

. THE HOPPER IS FILLED WITH TURNINGS

. A TITANIUM PRIMER IS PLACED IN THE CRUCIBLE

. FURNACE AND HOPPER ARE PUMPED DOWN THEN FILLED WITH ARGON

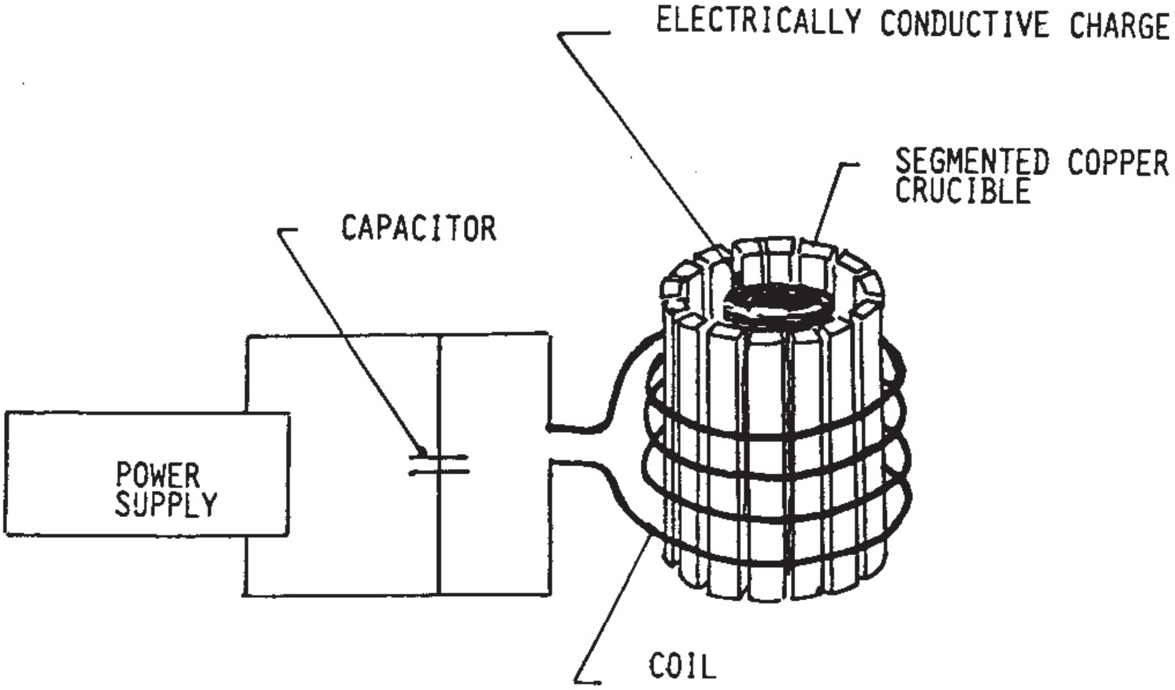
. THE OPERATING FREQUENCY IS SET BY SELECTING THE VALUE OF THE ADJUSTEMENT CAPACITOR

. THE POWER IS GRADUALLY TRANSMITTED UNTIL THE CHARGE MELTS AND FORMS A DOME

. THE SUPPLY OF TURNINGS AND THE SIMULTANEOUS CONTINUOUS EXTRACTION OF THE BILLET CAN BE STARTED.

DESCRIPTION OF THE PROCESS

PRINCIPLE



USE OF A SEGMENTED, WATER COOLED COPPER CRUCIBLE

- TO PROMOTE ELECTROMAGNETIC COUPLING WITH THE METALLIC CHARGE
- TO AVOID POLLUTION OF THE METAL

OPTIMISATION
FOR CONTINUOUS CASTING

THE CONTACT AREA BETWEEN LIQUID METAL AND CRUCIBLE IS AN IMPORTANT PARAMETER.

TOO LARGE ===> NO POSSIBLE BILLET EXTRACTION

TOO SMALL ===> METAL RUN-OUT

OPTIMISATION OF THE

- CRUCIBLE GEOMETRY
- COIL GEOMETRY
- ELECTRIC PARAMETERS

====>

. CONTINUOUS CASTING
WITHOUT SLAG
. HIGH TEMPERATURES

MUST TAKE IN ACCOUNT OTHER CHARACTERISTICS OF THE PROCESS.

- THE HEIGHT AND STABILITY OF THE DOME
- THE STIRRING
- THE MELTING RATE
- THE ENERGY EFFICIENCY

THREE EFFECTS

- THERMAL EFFECT (WHICH ALLOWS THE CHARGE TO BE MELTED)
- FIRST MECHANICAL EFFECT : PRESSURE WHICH DETERMINS THE FORM OF THE DOME
- SECOND MECHANICAL EFFECT : STIRRING OF THE METAL.

CHOICE OF THE FREQUENCY ===> FAVORISES ONE EFFECT.

DIMENSIONLESS PARAMETER "SCREEN PARAMETER" R

$R_\omega = \mu_0 \sigma \omega R^2$

WITH μ_0 MAGNETIC PERMEABILITY

σ ELECTRICAL CONDUCTIVITY

ω CURRENT PULSATION ($W = 2\pi F$)

F FREQUENCY

R CRUCIBLE RADIUS

CHARACTERISTICS VALUES OF R_ω

2 : VALUE FOR A PLANE FREE SURFACE

ELECTRICAL POWER

ADAPTED TO THE METAL AND TO THE MELTING RATE

NOT TOO STRONG ===> HIGH AND UNSTABLE DOME

$$H = \frac{B^2}{2 \mu_0 \rho g}$$

WITH

H	DOME HEIGHT
B	MAGNETIC FIELD IN THE CRUCIBLE
ρ	METAL DENSITY
g	GRAVITY CONSTANT
μ_0	MAGNETIC PERMEABILITY

METALLURGICAL

RESULTS

BILLETS OF EXCELLENT SURFACE QUALITY

(WHEN FREQUENCY AND POWER ARE CORRECTLY SELECTED)

NO CHEMICAL POLLUTION

WITH OXYGEN OR NITROGEN

WITH COPPER ===> THE CRUCIBLE IS NOT ATTACKED

6.4 ALLOY

	Al (%)	V (%)	Fe (ppm)	Cu (ppm)	O (ppm)	N (ppm)	C (ppm)
Turnings	6.2	4.1	1500	<50	2200	130	250
Billet	6.2	4.0	1550	<50	2250	120	260

NO LOSS BY VOLATILISATION

IN AL FOR 6.4. ALLOY

FINE EQUIAXED MACROSTRUCTURE

(EFFECT OF THE STRONG STIRRING)

CONCLUSIONS

. THE COLD CRUCIBLE CONTINUOUS CASTING IS A NEW PROCESS FOR THE INDUCTION MELTING OF REACTIVE AND REFRACTORY METALS AS TITANIUM.

. THE OPTIMISATION OF THE DESIGN AND OF THE ELECTRICAL PARAMETERS ALLOWS THE BILLETS CONTINUOUS DRAWING WITHOUT SLAG.

. BY MELTING TURNINGS, GOOD QUALITY BILLETS HAVE BEEN OBTAINED IN TITANIUM AND TITANIUM ALLOYS.(Ø < 150 MM   L = 2000 MM)

THEY HAVE THE QUALITY REQUIRED FOR A DIRECT TRANSFORMATION BY ROLLING OR EXTRUSION.

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STRUMENTI FINANZIARI A DISPOSIZIONE DELLE IMPRESE CHE PRODUCONO O UTILIZZANO IL TITANIO

Io vorrei ringraziare gli organizzatori del Convegno perché mi hanno consentito di intervenire e di non parlare di titanio, per lo meno direttamente. Credo, per quello che è l'amministrazione che rappresento, il Ministero dell'Industria, sia opportuno parlare degli strumenti finanziari che sono a disposizione delle imprese che producono ed utilizzano il titanio. Questo perché, in agosto, abbiamo approvato un nuovo piano energetico che, come voi sapete, esclude di fatto certe produzioni di energia elettrica, ribadisce certi concetti di importanza della conservazione dell'energia ed individua ulteriori strumenti per incentivare la conservazione dell' energia.

Prossimamente, probabilmente anche domani, il Consiglio dei Ministri approverà un disegno di legge di finanziamento per eseguire certi tipi di interventi. Interventi che hanno la finalità di contenere i consumi di energia nella produzione di manufatti e nel loro utilizzo, di ridurre i consumi specifici di energia nei processi produttivi, di favorire una più rapida sostituzione degli impianti in particolare nei settori a più elevata intensità energetica, anche attraverso il coordinamento tra le fasi di ricerca applicata, di sviluppo dimostrativo, di produzione industriale.

Credo che questo sia il disposto del primo articolo di questa futura legge e quindi credo che questo semplice fatto giustifichi il mio intervento.

Sicuramente oggi non stiamo ai concetti di risparmio energetico del decennio del ‘70, in cui l’idea era di non utilizzare una macchina che consuma energia e non stiamo neanche al concetto di conservazione dell’energia, che io direi dei primi anni dell’80, attraverso il quale si e avuto un impulso o per lo meno una volontà politica di diffondere tipologie (come ad esempio quella della congelazione) che utilizzano al meglio alcuni combustibili ma certo non risparmiano. Oggi siamo, credo, nel concetto del minore consumo specifico per unita di prodotto. Diverse altre esperienze che ci sono state, e ritengo siano note, hanno dimostrato che le azioni di risparmio non debbono favorire una diminuzione nella produzione, devono anzi favorirne l’aumento, che la quantità di risparmio e una funzione diretta del capitale investito nella situazione preesistente nel sistema impresa e che è anche possibile incentivare col denaro pubblico quest’iniziativa in funzione del risparmio atteso e dei benefici che la collettività più o meno direttamente ne riceverà.

L’esperienza ci ha anche dimostrato che l’energia può essere recuperata, può essere aggiuntiva oppure sostitutiva e questo mi pare sia molto importante (per quanto ho potuto sentire fino ad ora) proprio nel processo produttivo del titanio, perché l’esperienza ci ha dimostrato che l’impresa normalmente attribuisce all’energia ricuperata un valore economico che non dipende da fattori energetici, ma da altri fattori quali ad esempio il mercato, il prodotto, gli impianti e così via. Comunque l’iniziativa non è realizzabile, o perlomeno è realizzata con molte difficoltà, se modifica radicalmente il sistema di gestione preesistente e la conseguenza della politica energetica italiana, fino agli anni ‘85, è stata proprio questa: una serie di iniziative di recupero di energia, rapidissimo ritorno economico, con elevati valori di recupero.

Tuttavia nell’85 e nell’86 c’è stata una modifica nelle azioni di intervento da parte delle imprese industriali poiché si sono privilegiate le azioni che tendevano a modificare non l’impianto ma il processo, attraverso l’ottimizzazione della curva della domanda e dell’offerta dell’energia nell’ambito del sistema interno dell’impresa e ottimizzando le trasformazioni tra impresa e mondo esterno. Questo ha comportato investimenti molto più elevati, benefici energetici unitari inferiori, ma tempi di vita dell’intervento maggiori, perché il tempo di vita dell’innovazione tecnologica non è sicuramente legato alla sola vita fisica dell’impianto ma è legata anche alla vita della innovazione tecnologica del prodotto. Di conseguenza, si è venuta a creare quella coincidenza di interesse, tra impresa e collettività, a realizzare azioni di conservazione di energia.

C’è anche da dire che uno dei grossi problemi della politica della conservazione dell’energia è che un’impresa non ha mai la ragione sociale di risparmiare energia (la società Ginatta ha la ragione sociale di produrre titanio non di risparmiare energia) e uno dei nodi fondamentali, è quello di coinvolgere direttamente, come strumento attivo di risparmio, le imprese industriali che hanno finalità diverse. Come fare per ottenere questo? Probabilmente si dovrebbe intervenire sul mix di prodotti lavorati e semilavorati, e qui interviene la valenza di risparmio virtuale del titanio perché resiste alla corrosione, ha dei pregi chimico-fisici sicuramente superiori a quelli dei materiali a cui va sostituito e comunque si ripaga nel tempo.

L’altro problema é quello di intervenire non solo come si é fatto adesso sugli utenti finali che acquistano gli oggetti, l’uso civile, i trasporti e così via, ma tentare di intervenire in maniera incisiva sulle imprese che producono i manufatti tramite i quali altri conseguiranno il risparmio energetico e questo mi pare sia il terzo e conclusivo punto del discorso.

Per fare questo, per potere intervenire in maniera incisiva, questa nuova legge che vi ho citato favorisce non a caso certe particolari tipologie. Le favorisce dando contributi in conto capitale per un x% fino ad un massimo del 50%, non incentivando impianti dimostrativi (io dico sempre che nessuno di noi si comprerebbe un'automobile dimostrativa e anche se l'avesse in regalo probabilmente la userebbe con estrema cautela solo perché gli è stata dichiarata dimostrativa), ma incentivando impianti che sono nuovi per gli aspetti tecnici, direzionali, organizzativi nonché tecnologie, e questo credo sia il punto di maggior interesse in questo momento d'incontro, che hanno bisogno di ulteriori strumenti economici e finanziari per raggiungere la maturità commerciale o di esercizio, con obiettivo di ridurre il tempo di ritorno globa1e degli investimenti.

Il costo dell'energia oggi è basso ma domani non lo sarà perché, non solo non dipenderà da fatti interni nazionali, ma perche il libero mercato del '92 sicuramente ci porterà a confrontare la struttura dei nostri prezzi di energia con la struttura dei prezzi della Comunità Europea, sotto l'ottica di una maggiore trasparenza, con il risultato globale che il prezzo dell'energia tenderà ad aumentare.

A questo punto l'altro parametro per un calcolo sempre intorno all'investimento è l'investimento stesso, che va misurato sul tempo di vita dell'impianto, sulla sua capacità di non invecchiare o comunque di essere esercito al massimo della sua potenzialità, e quindi credo che effettivamente anche il titanio, che come l'alluminio è sempre stato visto così come un nemico dai risparmiatori di energia, possa e debba viceversa essere considerato come uno dei tanti elementi che concorrerà a una corretta politica energetica italiana.

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APPLICAZIONI DEL TITANIO NELLA PROTEZIONE CATODICA DI GRANDI OPERE IN CEMENTO ARMATO

Voi sapete che le armature nel cemento armato sono perfettamente protette dall'alcalinità del calcestruzzo quindi nella stragrande maggioranza dei casi non ci sono problemi di corrosione. Ci sono però alcune situazioni particolari, e alcune di queste estremamente importanti, in cui la corrosione dell'armatura avviene. La più importante di queste condizioni è quella che si ha sui ponti delle autostrade dove nei mesi invernali si mette il sale per evitare la formazione di ghiaccio; i cloruri penetrano e le condizioni di passività che normalmente difendono le armature dalla corrosione vengono meno e quindi si ha un attacco estremamente forte in maniera localizzata o generalizzata a seconda dei casi. Si pensi che le opere di manutenzione sono quasi tutte dovute, almeno nei tratti appenninici o alpini, alla corrosione delle armature. L'unica tecnica che ha dimostrato di essere in grado di bloccare la corrosione dai cloruri è la protezione catodica. Che cos'è la protezione catodica? la protezione catodica è una tecnica vecchissima, molto più vecchia del cemento armato. Ha la stessa età del portland però è arrivata alla protezione del cemento armato solo da dieci anni. In Fig. 1 è schematizzata da una parte l'armatura, dall'altra un anodo: la tecnica della protezione catodica mediante la quale si può far passare una corrente dall'anodo all'armatura in senso catodico, cioè nel senso che l'armatura funziona da catodo mediante un raddrizzatore esterno. Con un elettrodo di riferimento si controlla che tutte le cose siano fatte bene.

La tecnica è largamente diffusa nel campo della protezione delle strutture interrate e delle strutture a mare. Perché è difficile proteggere le armature? Perché l'elettrolita é il calcestruzzo e questo ha il grosso inconveniente di essere prima di tutto un cattivo conduttore, e, in secondo luogo, per motivi geometrici: nell'acqua di mare o nei terreni l'anodo si può mettere lontano dalle strutture da proteggere, nel caso invece delle strutture in cemento armato l'anodo va posto in superficie della struttura stessa e la protezione catodica si può avere solo se si riesce a distribuire uniformemente la corrente su tutta la struttura. La corrente per la protezione catodica è bassissima: 5,10 mA/m^2 secondo i casi, per proteggere un ponte di 1000 m^2 bastano 20 Watt, meno di una lampadina. Ecco una brevissima storia degli ultimi 10 anni della protezione catodica per capire dove è nata, come è nata, come si è sviluppata:

- 1974: dopo l'esperienza di Straff in America la Federal Highway Administration, che è l'ente americano che deve controllare tutti i problemi delle autostrade, propone di utilizzare un sistema di protezione catodica ed ha utilizzato sostanzialmente questo sistema (Fig. 2): sulla soletta dei ponti mette uno strato conduttivo di 10 cm, c'è un conduttore che porta la corrente a questo strato conduttivo di asfalto (l'asfalto è reso conduttivo mediante aggiunta di carbone) poi sopra viene messo un altro strato. I grossi problemi di peso, i grossi problemi di consumo ecc ... fanno sì che questa soluzione, che è ottima dal punto di vista elettrochimico, di fatto non soddisfi. Sono un'ottantina i ponti che sono andati in funzione dal 1974 al 1980; tutti funzionano, vanno bene, ma lo strato deve essere rifatto ogni tanto.

- 1978-‘79: viene cambiata la tecnica. Vengono fatte delle scanalature nel ponte (Fig. 3), vengono messi dei fili di titanio platinato (quasi tutti), in qualche caso di Nb platinato. Vi sono dei grossi problemi di distribuzione di corrente; questa tecnica all’inizio non va bene, poi la migliorano un po’ ma non soddisfa.

- 1982: la Federal Highway Administration esce con l’affermazione che dà un impulso a tutto il programma, dice:"l’unica tecnica" che è in grado di bloccare la corrosione sui ponti è, indipendentemente dal tenore dei cloruri, la protezione catodica. Le al tre tecniche, (le cita tutte) hanno dato risultati poco soddisfacenti. Era da 10 anni che la Federal Highway Administration portava avanti le esperienze in questo campo.

- 1983: ecco il primo "salto". Viene utilizzato come anodo non più uno strato conduttore come prima, ma una struttura anodica filiforme di materia plastica (Fig. 4) con un’anima di rame resa conduttrice mediante l’aggiunta di carbone, distribuita su tutta la superficie del materiale metallico, che viene posta sopra le armature (ovviamente tra le armature e questo anodo ci deve essere del calcestruzzo) e poi viene ricoperta con uno strato di asfalto. La cosa funzionò bene dal punto di vista elettrochimico per quanto riguardava la distribuzione di corrente ma dopo qualche anno il carbone iniziava a consumarsi. Infatti è noto che il carbone ed il calcestruzzo in ambiente alcalino quando funzionano da anodo bruciano.

- 1985, 3 anni fa; entra il titanio e in poco tempo si affianca e poi spiazza tutti i sistemi precedenti i quali funzionano, perché sono stati applicati, ma il futuro è quello degli anodi di titanio.

La rete di titanio (Fig. 5) posta sopra le armature é collegata con il polo positivo di un generatore di corrente, il polo negativo è ovviamente collegato con le armature e il tutto viene ricoperto con uno strato di asfalto. In America mettono del calcestruzzo direttamente sopra, in quanto sui ponti non c'è strato di asfalto.

Quali sono i vantaggi di questa rete di titanio? Innanzitutto il titanio non è titanio soltanto, ma è titanio ricoperto di un film sottilissimo di ossidi vari, tipo ossido di rutenio. Questo titanio è in grado di erogare corrente a bassa tensione senza consumarsi. L'esperienza che si sta facendo a Milano ha dimostrato che anodi di questo tipo (che ormai hanno erogato una carica corrispondente a quella che alle condizioni di esercizio viene erogata in più di 30 anni) sono ancora perfetti. Le reti sono diverse, ci sono 3 o 4 produttori di queste reti a livello mondiale. Al Politecnico di Milano utilizzano le reti DeNora e gli esempi che verranno dopo sono tutti esempi relativi a questo tipo di rete.

La rete di titanio si ottiene da una lamiera in titanio molto sottile (0.5, 0.6 mm) che viene espansa. E' una rete molto leggera che viene fissata normalmente se viene applicata su parete verticale oppure, se viene applicata sul soffitto, si utilizzano dei sistemi di plastica.

Per distribuire bene la corrente ci sono dei portatori di corrente (Fig. 6), sempre di titanio, che vengono messi sulla rete. Essa non deve mai lavorare a correnti elevate; nel caso in cui sia necessario, perché c'è un'alta densità di armature, per erogare una corrente più alta è opportuno fare la maglia più piccola oppure, cosa che in genere è più semplice, si mettono due reti una sopra l'altra (Fig. 7).
I processi anodici sono diversi nel caso che si usi titanio rispetto ai casi a base di materiale carbonioso (Figg. 8 e 9).

Qui si parla solo del comportamento anodico. In effetti il sistema andrebbe analizzato dall'anodo al catodo ma qui interessa la situazione del titanio quindi la nostra attenzione è focalizzata su questo. La sovratensione anodica è molto più bassa nel caso del titanio. Tra l'anodo di titanio e l'anodo a base di carbonio c'è una differenza piuttosto alta di 0,6, 0,7, 0,8 Volt (Fig. 10).

Alcuni esempi: come detto all'inizio, il caso più diffuso di protezione catodica con reti di titanio è quello delle solette dei ponti allora io vorrei fare un altro esempio diverso da quello delle solette di cui l'Ing. Grandi parlerà dopo di me.

Fig. 11 mostra il supporto di un agitatore in Arabia, che ogni due anni andava cambiato. C'è un'alta densità di armature, ed é stato tolto tutto il calcestruzzo (Fig. 12). Viene prima fatta la gettata che copre tutte le armature poi viene posta la rete (Fig. 13). Se ci sono delle situazioni locali, ad esempio un foro, ovviamente bisogna sistemare opportunamente la rete. E' molto semplice: la si taglia con le forbici, la si mette sopra tutto, la si ricopre completamente con il calcestruzzo e l'opera è finita. Naturalmente bisogna far passare corrente; in questo caso la tensione applicata é molto bassa: 2,2 Volt.

Caso di un garage (Fig. 14): qui le armature sono corrose, il rosa della fotografia sta ad indicare che la corrosione non è da carbonatazione ma è da cloruri. A metà dell'opera la rete viene stesa sul pavimento e poi si stende l'ultimo strato di calcestruzzo. Sul soffitto si fa la stessa operazione.

Tutte le applicazioni di questi esempi sono state fatte l'anno scorso, due anni fa e quest'anno.

Fig. 15 mostra una villa in Florida: c'è presenza di cloruri perché ci fu un errore iniziale, venne usato il calcestruzzo fabbricato con sabbia di mare che causò problemi di corrosione molto grossi. Il problema é stato risolto fissando la rete su una parete verticale, con anelli di plastica. In Fig. 17 si vede la spruzzatura finale sulla parete verticale.

Esempio in Arabia; questo tra l'altro è un test che poi non è andato in esercizio, anzi qui c'è stato un insuccesso. Questo è un grosso canale per l'adduzione dell'acqua di mare (Fig. 18), dove ci sono problemi di corrosione. L'operazione che è stata fatta molto male è stata quella di pulizia della superficie che deve essere pulita interamente. Attenzione! La superficie va pulita togliendo solo il calcestruzzo che si stacca e non quello contenente i cloruri. Mentre con tutte le altre tecniche per ripristinare le strutture in cemento armato bisogna togliere tutto il calcestruzzo che contiene cloruri (anche quello "sano" meccanicamente), pena l'insuccesso completo del sistema, in questo caso i cloruri vanno benissimo, infatti in caso di protezione catodica aumentano la conducibilità, alcuni anzi sostengono di metterli, io sono restio per motivi psicologici a far mettere i cloruri, ma i cloruri non danno nessun problema dal punto di vista della corrosione (qui si tratta sempre di una parete verticale, si vedono gli anodi ed i sistemi per fissarli alla parete. La parete é stata coperta di calcestruzzo e poi è stata ionizzata). L'operazione è fallita, perché (e questo è uno dei problemi delicati) la preparazione della superficie non è stata fatta bene e lo strato successivo non è stato ben ancorato alla parete con opportuni sistemi, di conseguenza si è staccato tutto il sistema. Questo per dire che il punto delicato, il punto debole di questa protezione non è il sistema anodico.

Ultimo esempio: vicino a Lugano sulla ferrovia del Gottardo hanno deciso di proteggere due pilastri, anche questi inquinati da cloruri, che sono cavi. Uno viene protetto dall'esterno, l'altro viene protetto dall'interno (Figg. 19,20,21).
Il pilastro che sarà protetto dall'esterno viene pulito, sabbiato (spesso si usa la idrosabbiatura per togliere lo strato superficiale e per far ancorare bene lo strato successivo) poi si fa il collegamento catodico. Naturalmente il

negativo del generatore deve essere collegato con le armature, fra l’altro occorre vedere che le armature siano connesse tra di loro (cosa che viene fatta preliminarmente).

L’altro pilastro invece di essere protetto dall’esterno é stato protetto all’interno utilizzando lo stesso sistema.

Con questi esempi recenti concludo il mio intervento ringraziando la Società DeNora che ha permesso di illustrare le sue realizzazioni.

Grazie.

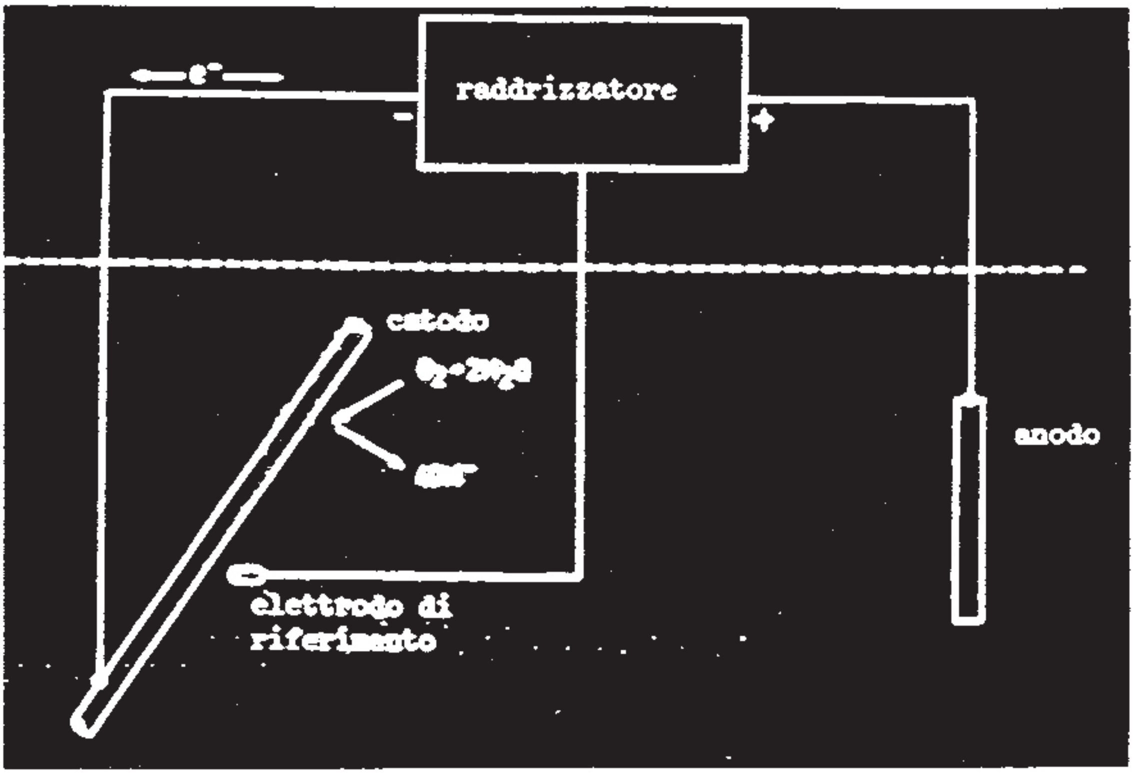
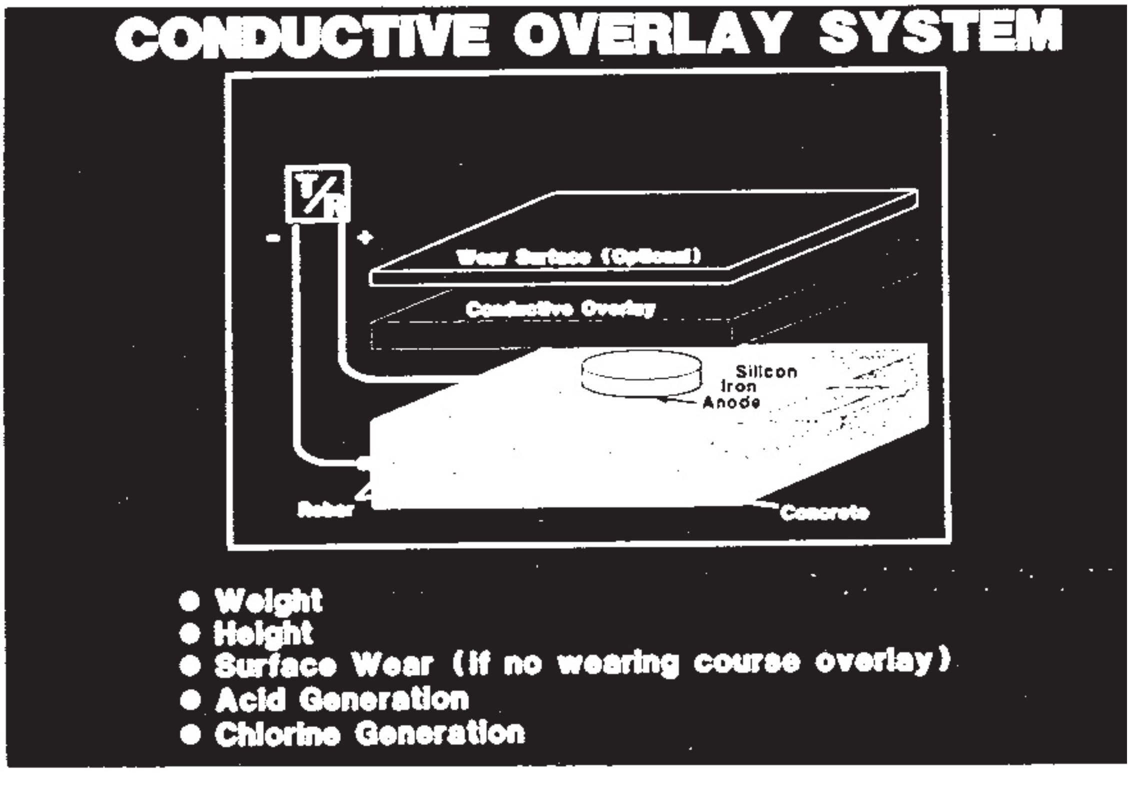
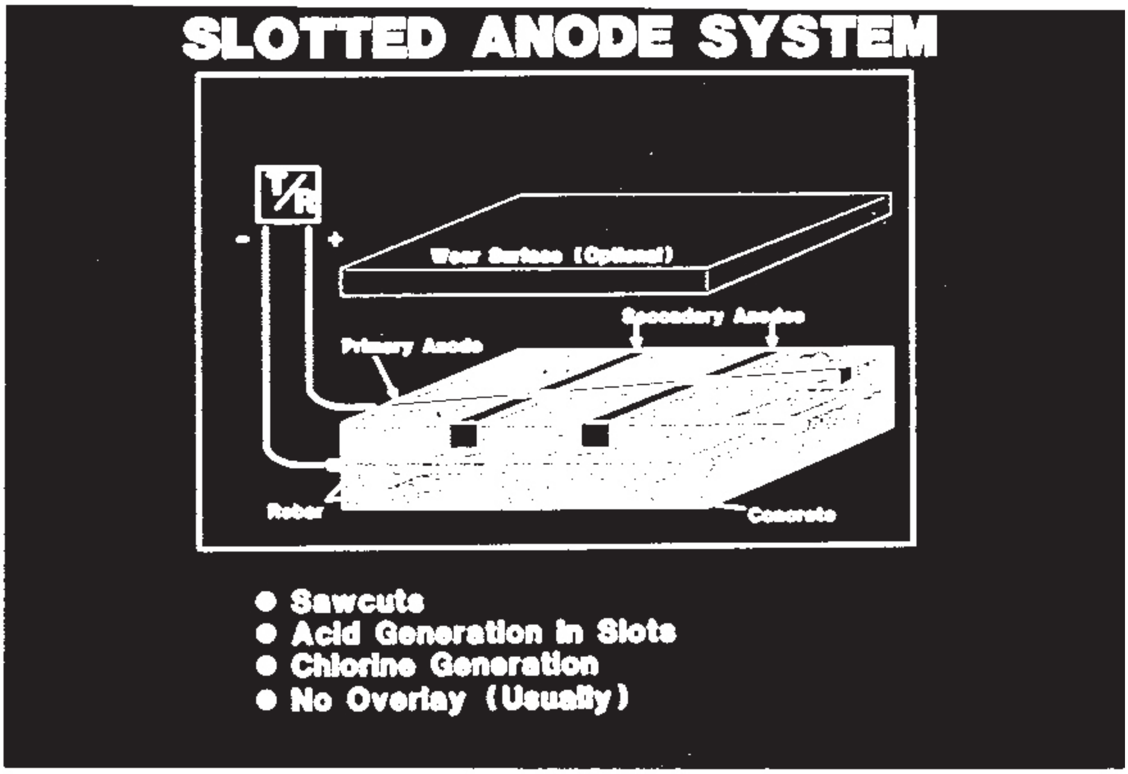


Fig. 1 - Schema di funzionamento della protezione catodica


CONDUCTIVE OVERLAY SYSTEM

- Weight
- Height
- Surface Wear (if no wearing course overlay)
- Acid Generation
- Chlorine Generation

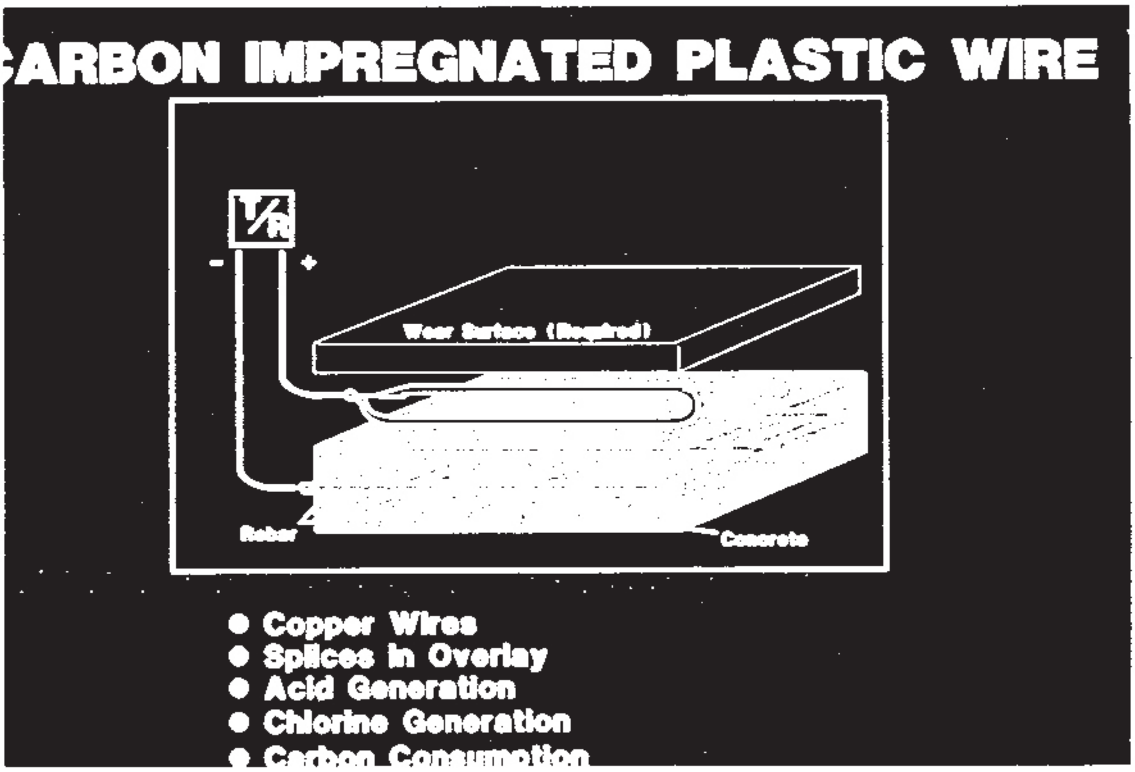
Fig. 2 - Sistema di protezione catodica con strato conduttivo



SLOTTED ANODE SYSTEM

- Sawcuts
- Acid Generation in Slots
- Chlorine Generation
- No Overlay (Usually)

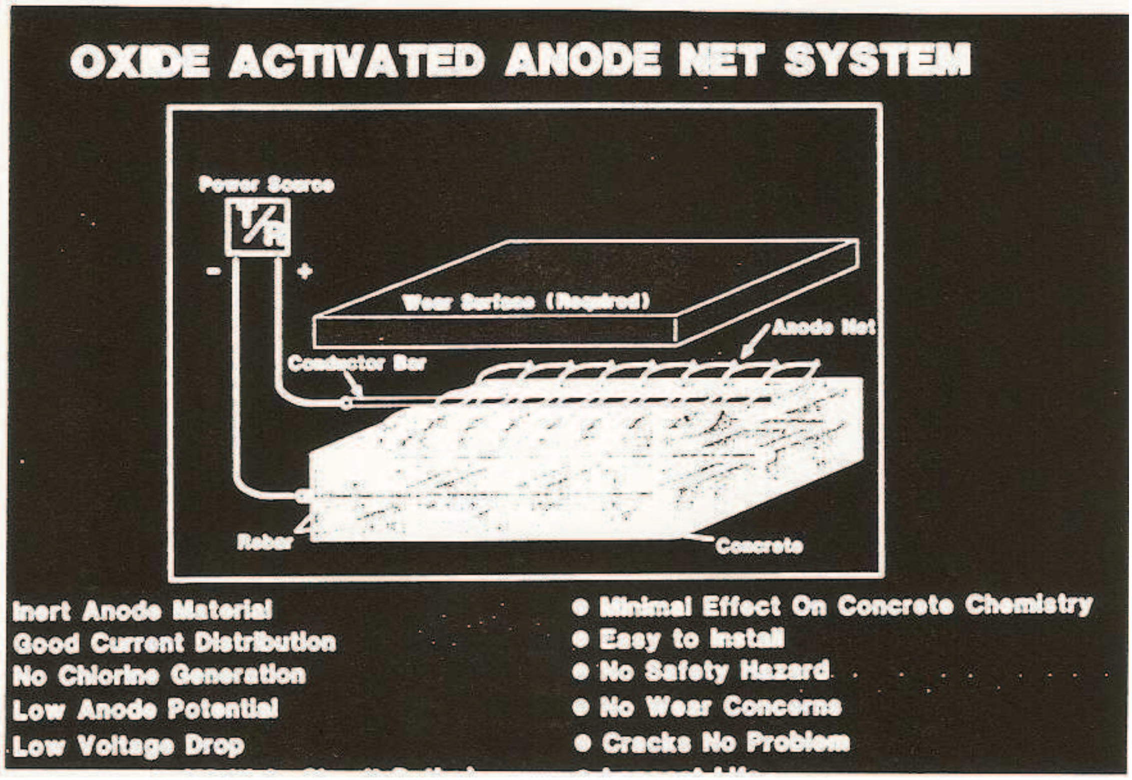
Fig. 3 - Protezione catodica con fili di titanio



ARBON IMPREGNATED PLASTIC WIRE

- Copper Wires
- Splices in Overlay
- Acid Generation
- Chlorine Generation
- Carbon Consumption

Fig. 4 - Protezione catodica con filo plastico conduttivo



OXIDE ACTIVATED ANODE NET SYSTEM

Inert Anode Material
Good Current Distribution
No Chlorine Generation
Low Anode Potential
Low Voltage Drop

- Minimal Effect On Concrete Chemistry
- Easy to Install
- No Safety Hazard
- No Wear Concerns
- Cracks No Problem

Fig. 5 - Protezione catodica con rete di titanio

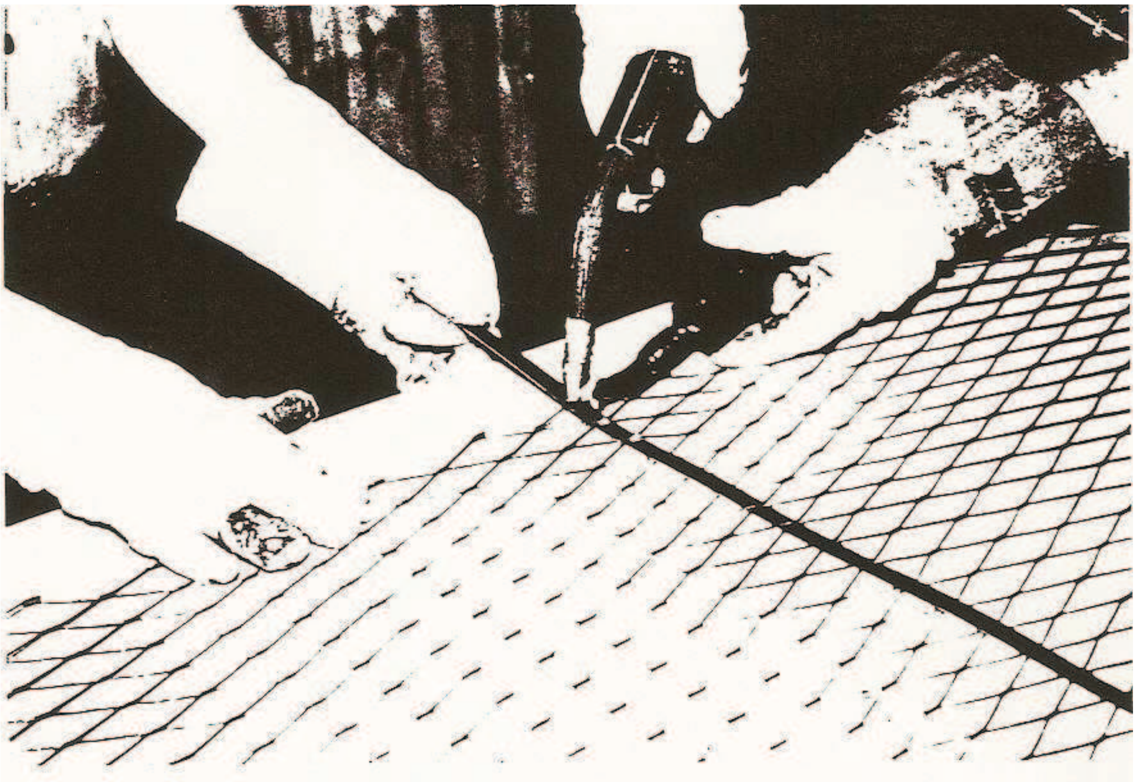


Fig. 6 - Preparazione reti di titanio

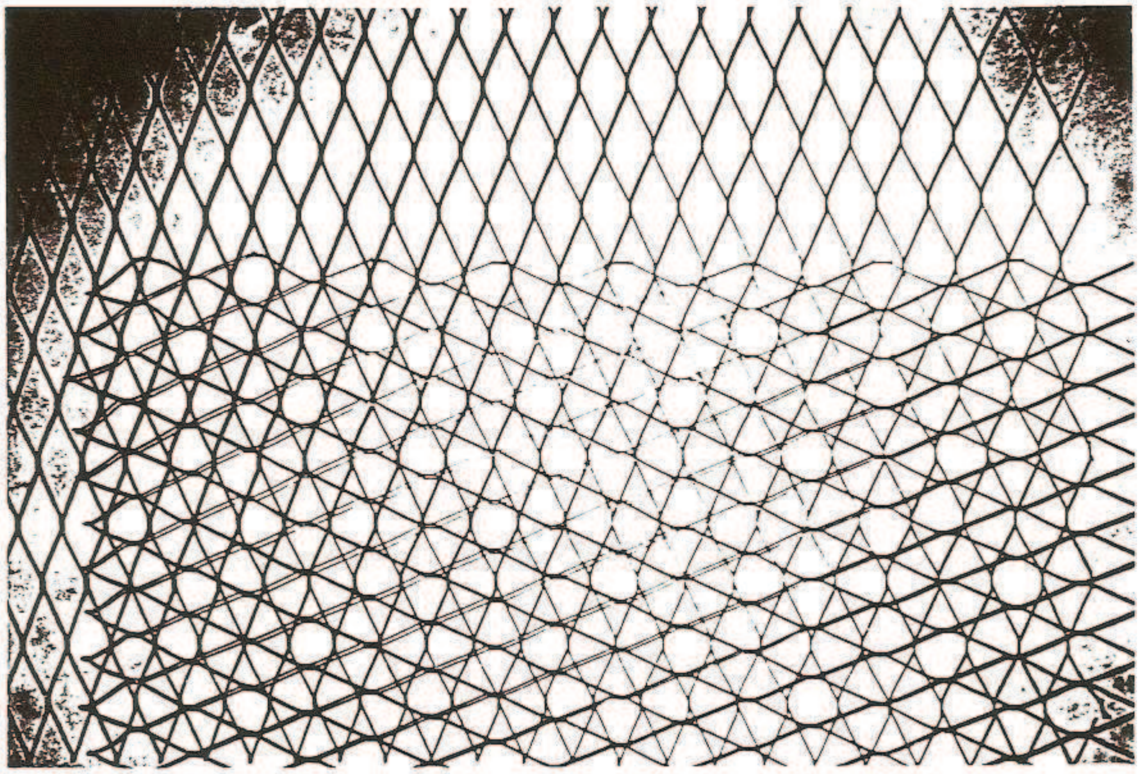
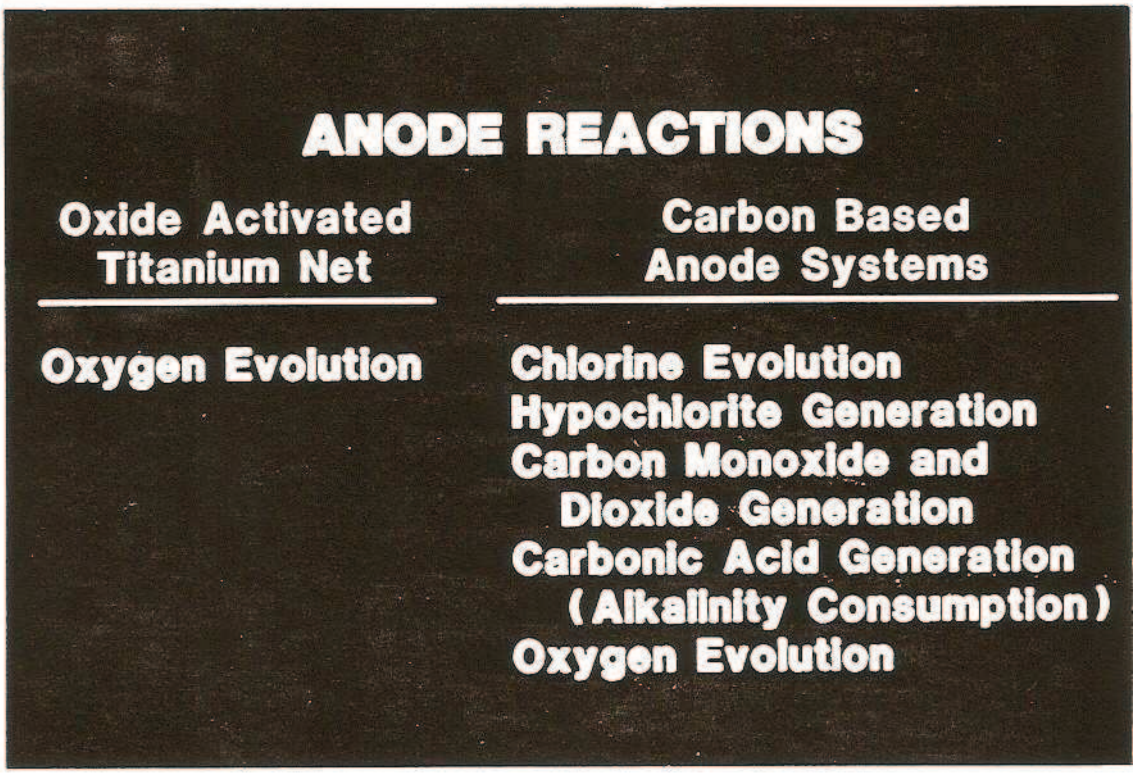


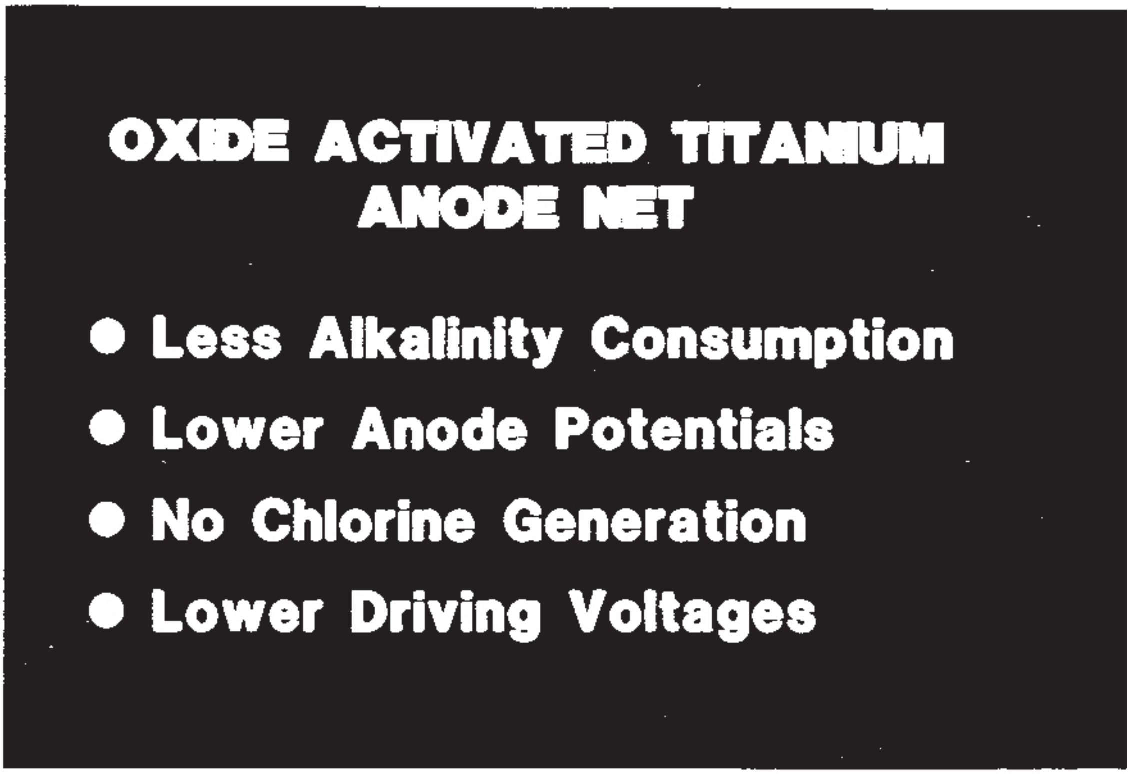
Fig. 7 - Sistema usato per aumentare la densità di corrente



ANODE REACTIONS

Oxide Activated Titanium Net	Carbon Based Anode Systems
Oxygen Evolution	Chlorine Evolution Hypochlorite Generation Carbon Monoxide and Dioxide Generation Carbonic Acid Generation (Alkalinity Consumption) Oxygen Evolution

Fig. 8 - Reazioni anodiche nei diversi sistemi



OXIDE ACTIVATED TITANIUM ANODE NET

- Less Alkalinity Consumption
- Lower Anode Potentials
- No Chlorine Generation
- Lower Driving Voltages

Fig. 9 - Vantaggi degli anodi in titanio

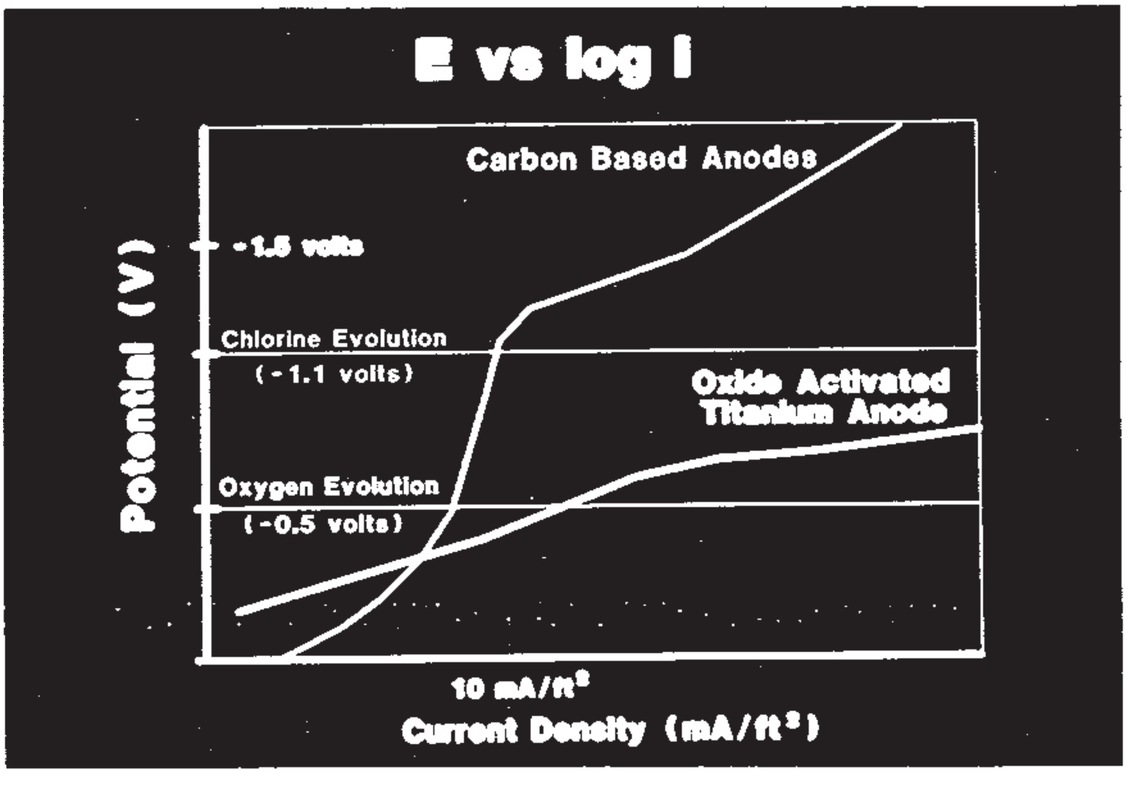


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Fig. 10 - Sovratensioni anodiche nei casi di anodi di titanio ed anodi a base carbonio

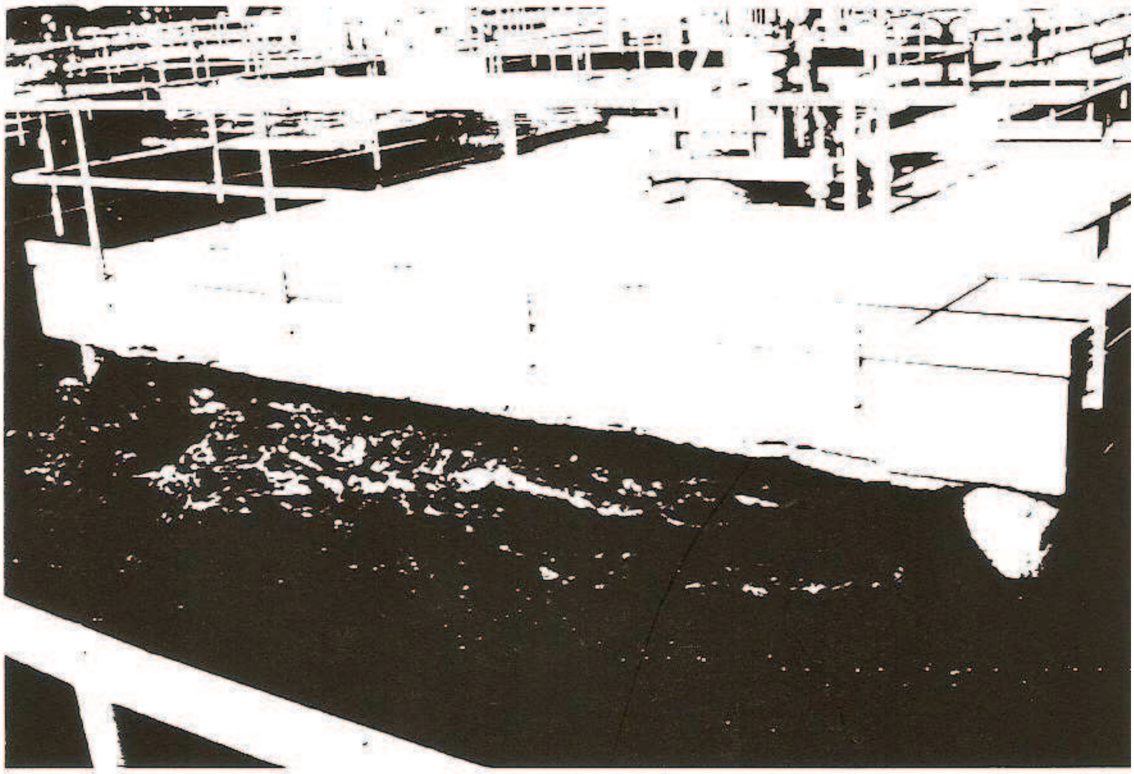


Fig. 11 - Supporto agitatore impianto

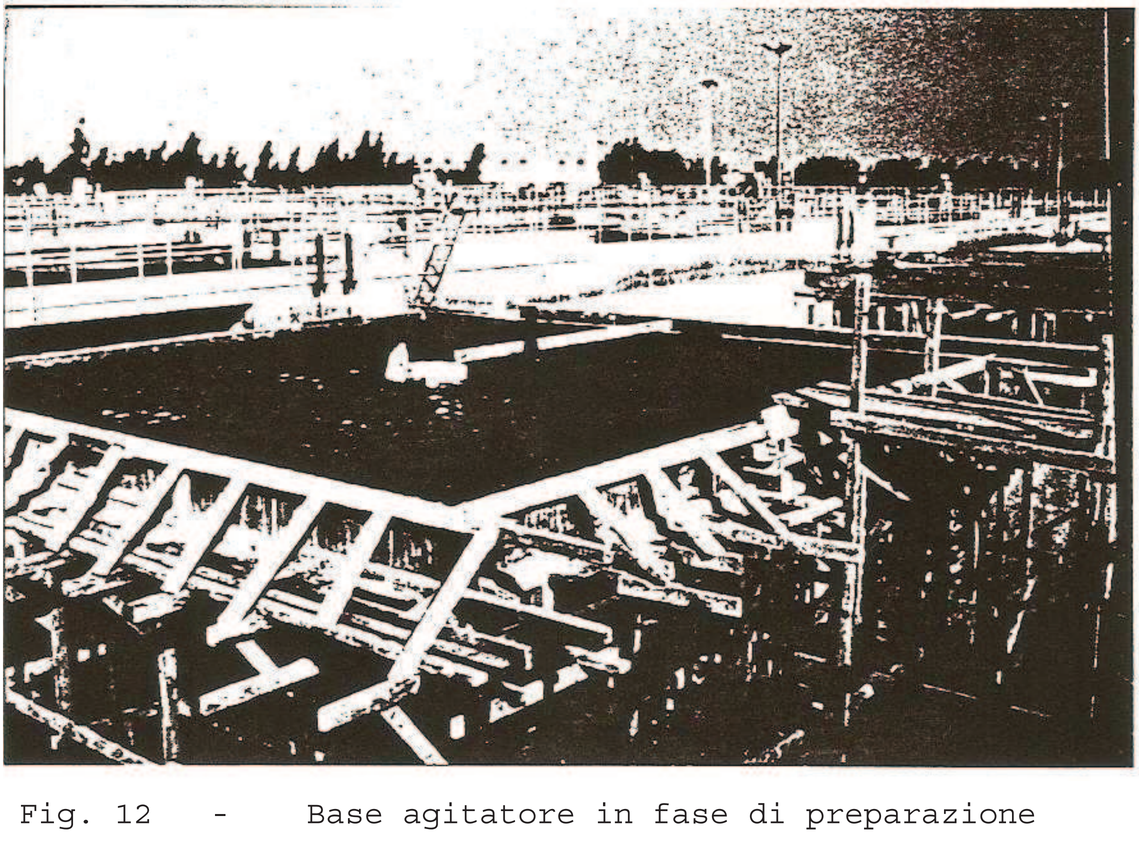


Fig. 12 - Base agitatore in fase di preparazione

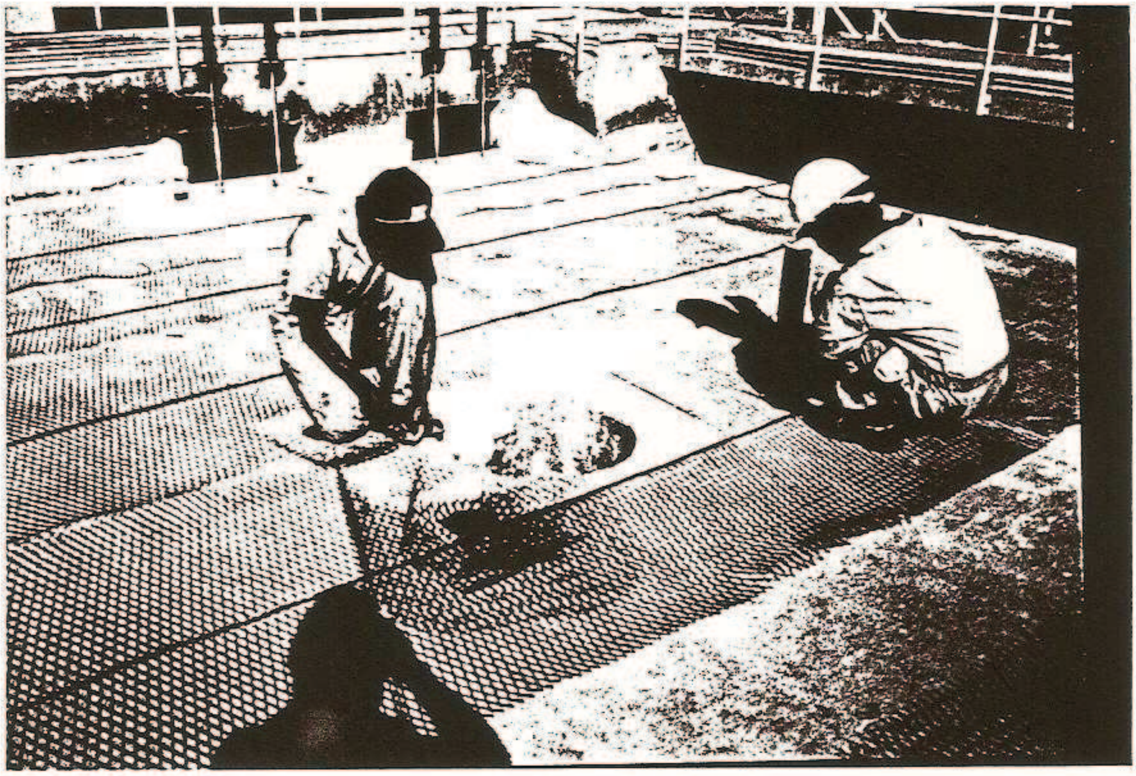


Fig. 13 - Posizionamento reti di titanio

Fig. 14 - Corrosione armature di un garage

Fig. 15 - Villa in Florida

Fig. 16 - Fissaggio rete in titanio con anelli di plastica

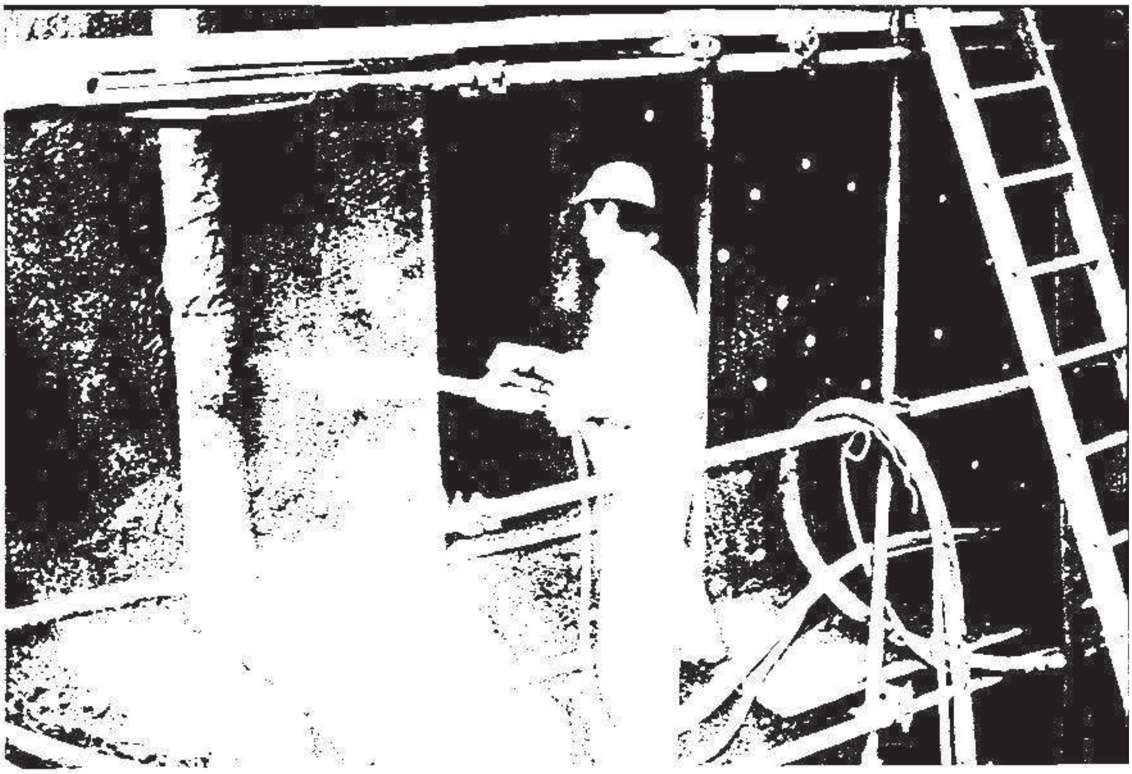


Fig. 17 - Spruzzatura finale sulla parete verticale

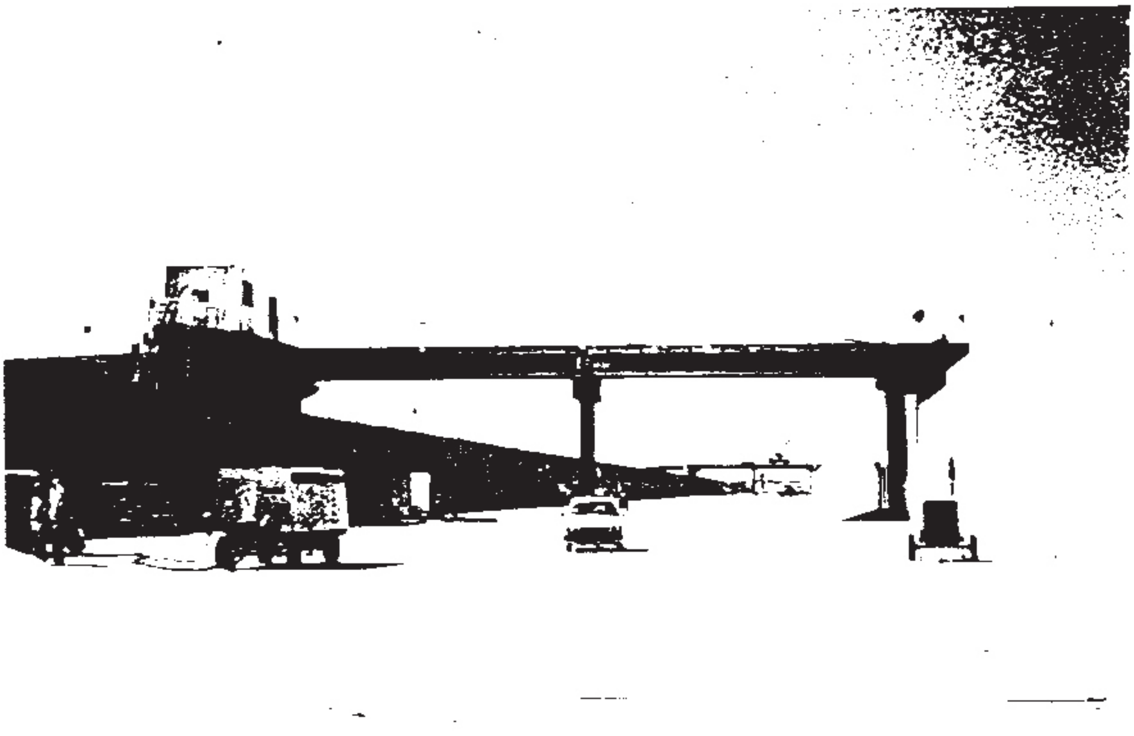


Fig. 18 - Canale di afflusso per acqua di mare in Arabia Saudita

Fig. 19 - Ferrovia del Gottardo - Piloni da proteggere

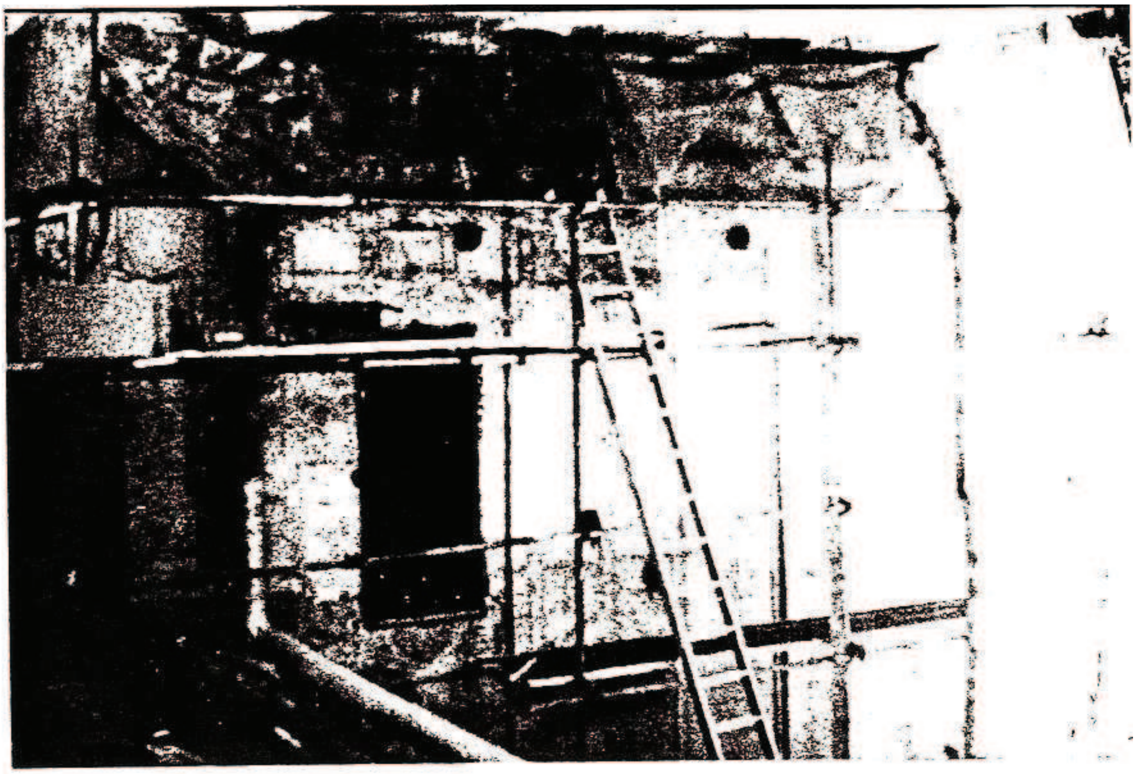


Fig. 20 - Protezione esterna mediante reti in titanio

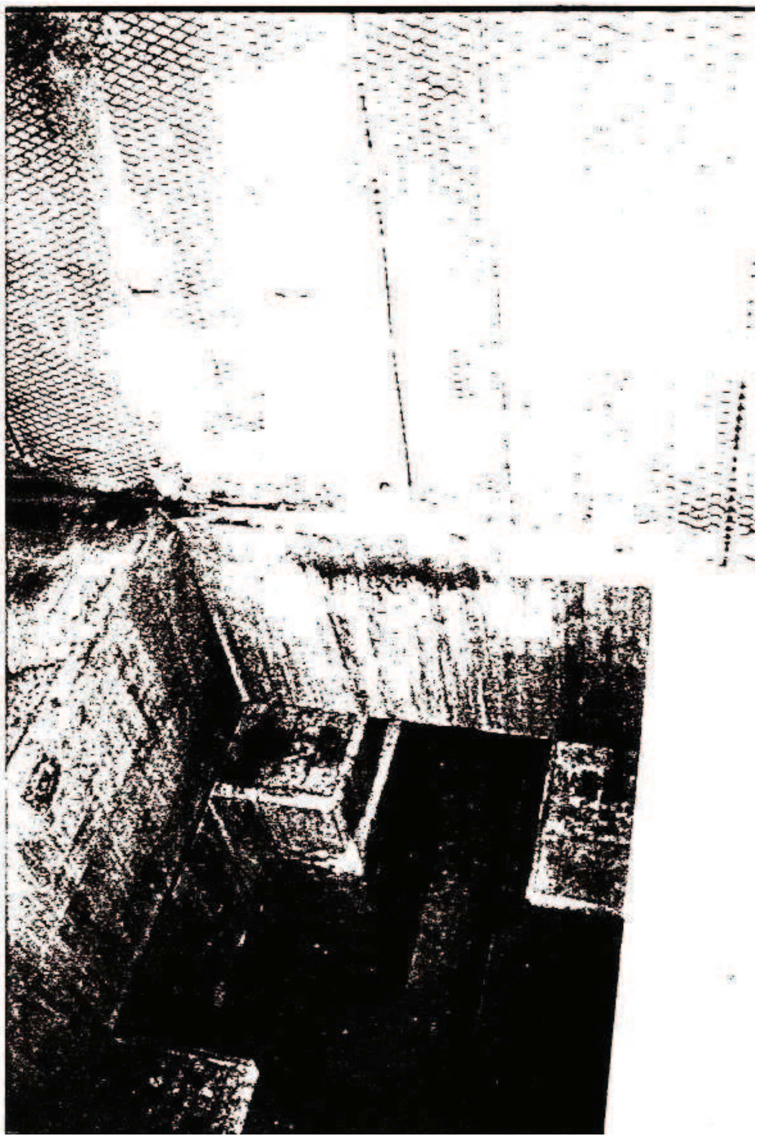


Fig. 21 - Protezione interna della struttura

Antonio Grandi
Nuova Polmet, Italia

PROTEZIONE CATODICA DEL CEMENTO ARMATO E CEMENTO ARMATO PRECOMPRESSO CON ANODI AL TITANIO ATTIVATO NUOVA POLMET-ELGARD: UN MERCATO IN SVILUPPO - PRIME APPLICAZIONI E PROSPETTIVE.

Buongiorno a tutti, io sono Grandi della Nuova Polmet. Come ha detto Pedeferri presenteremo quelle che sono le nostre applicazioni sostanzialmente sui viadotti dei ponti. Abbiamo gradito molto essere presenti a questo convegno per 2 ragioni: primo perché quale migliore occasione di poter presentare la nostra tecnologia in un convegno sul titanio, dato che proprio il titanio fa la parte di qualificante della nostra tecnologia e secondo perché direi che è proprio la città di Torino che forse ha valorizzato di più questa tecnologia con la Società S.I.T.A.F., la Società Italiana per il Traforo Autostradale del Frejus, che ci ha affidato la realizzazione della protezione catodica su delle opere molto importanti.

Possiamo vedere infatti subito la prima diapositiva (Fig. 1): questo lavoro è in corso d'opera; questo è il ponte, il viadotto Giaglione. Installeremo la protezione catodica su tutti i ponti del terzo lotto che sono ponti lunghi 600-700 m ciascuno e sono ponti organizzati a conci.
Fig. 2 mostra i conci preparati in attesa di varo del viadotto Clarea, quello successivo molto vicino a Giaglione, come si vede sono elementi prefabbricati che vengono poi varati con opportuni carroponti sulle pile già costruite.
In fig 3 si vede ancora l'area di prefabbricazione, si vede il concio prima del getto, si vede quanto sia densa l'armatura molle da intendersi la materia non precompressa dei conci. Fig. 4 è ancora il viadotto Giaglione, questo è già stato montato e si vede la prospettiva di tutto il viadotto.

Fig. 5 è la movimentazione dei conci; dopo la produzione ogni concio di questo pesa circa 40-60 t, forse dà un'idea di quella che è l'importanza dell'opera.
Come ha detto Pedeferri il ferro nel cemento armato, purtroppo per la nostra società, sta benissimo salvo in presenza di cloruri.
Sono i cloruri che vengono o dall'ambiente marino oppure da impasti sbagliati come quello che è avvenuto nella villetta della Florida presentata da Pedeferri oppure, sostanzialmente, dai sali antigelo. Possiamo dare questi dati: negli U.S.A. circa il 40% dei ponti autostradali, che sono circa 530.000, sono considerati già pesantemente attaccati dalla corrosione. Tanto per dare un altro dato (poiché penso sia abbastanza efficace) sul tratto appenninico della Bologna-Firenze vengono sparse ogni anno 50.000 t di sale. Questo è utilizzato proprio per evitare, se vogliamo, gli spalaneve.
Statisticamente si può dire che in Italia, in pianura, una struttura, un viadotto, può durare da 15 a 20 anni, in montagna la durata si riduce a 5 o a 10, in Svizzera a 5 o a 10 lo stesso, abbiamo casi particolari come S. Bernardino che sono 7 anni, negli U.S.A. dove non si fa uso di asfalto sulle solette dei ponti ecco che la vita cade a 3-5 anni dalla realizzazione (Fig. 6).

Quali sono le tecniche di prevenzione? Le più vecchie sono i nitriti di calcio, le membrane, il rivestimento dei ferri, il miglioramento del rapporto con il cemento durante l'impasto che fa si che si possa avere un cemento meno poroso e quindi meno permeabile ai cloruri, e direi la protezione catodica di cui ha parlato Pedeferri (Fig. 7).

Nel 1975 sono nate le reti a titanio attivato, nel 1987 la prima applicazione è stata la nostra in Italia proprio sul tratto autostradale per conto della Società Autostrade tra Sasso Marconi e Violeggio.

La nostra società fa uso delle reti al titanio della Elgard americana. 50.000 m^2 di protezioni catodiche sono già installate, 25.000 sono in fase di installazione. Cosa fa la corrosione? Fig. 8 mostra esempi eclatanti: vediamo la corrosione localizzata, teniamo presente che questi sono i ferri che sono rimasti dopo la demolizione completa o quasi della soletta e quindi sono considerati ancora tutto sommato accettabili.

La sequenza di installazione dell'impianto è la seguente: idrodemolizione della soletta, circa 3/4 dello spessore, rimozione, sostituzione di tutte le armature e installazione degli elettrodi di riferimento nel nuovo getto che è stato fatto, installazione delle sonde galvaniche che sono altri elettrodi che servono per la misura della efficacia della protezione catodica, ripresa del calcestruzzo fino a coprire 2-3 cm della parte superiore dell'armatura, posa della rete al titanio e finitura del getto con altri 2 o 3 cm di calcestruzzo.

In Fig. 9 si possono vedere tutti i cavi che fuoriescono dalla parte sottostante della soletta relativi agli elettrodi di riferimento; elettrodi di riferimento che misureranno il potenziale della struttura per verificare se la struttura è in protezione.

Fig. 10: le reti vengono appaiate e stese su tutta la superficie del ponte.

Fig. 11: è l'operazione di saldatura della piattina al titanio che dà continuità ai vari rotoli di anodo e che fuoriuscendo dalla soletta verrà poi collegata al cavo positivo che andrà all'alimentatore.

Fig. 12: l’operazione finita dà un’idea abbastanza chiara della situazione. Dopodiché aspettando non più di 2, 3, 4 h. al massimo, dipende poi dalle condizioni ambientali, proprio per il problema dell’aderenza tra il getto finale di calcestruzzo e quello sottostante si finisce il getto. Ripeto che è molto importante fare l’operazione velocemente per essere sicuri che si formino sotto e sopra la rete di titanio un conglomerato monolitico. Come si vede nella parte dietro della diapositiva ci sono le reti stese e gli operatori, che a mala pena camminano sul getto ancora fresco, stanno finendo l’operazione del getto.

L'’altra campata, la carreggiata in direzione Nord, essendo stata organizzata da noi quest’estate, presentava il problema che, aspettando anche solo 2 o 3 h, con temperature elevate quali quelle che si registravano verso giugno si temeva che il cemento maturasse troppo e quindi non si avesse l’adesione perfetta tra il sottostrato e l'’ultimo getto. Allora la Società Autostrade ha deciso di completare la soletta del ponte e darci il ponte solo a ripristino effettuato. A nostra cura prevedere un materiale particolare di copertura delle rete. Questo trattamento superficiale però riguarda proprio il rendere rugosa la superficie per un perfetto ancoraggio dell’overlay. Questa è una pallinatura, una macchina che ad alta velocità "spara" sulla superficie delle palline d’acciaio che poi vengono raccolte per non lasciare la superficie "inquinata".

Fig. 13: siamo sul Clarea. E’ lo stesso procedimento: qui stanno rifinendo a mano le zone che con la macchina non sono state eseguite bene qui lavoriamo applicando la protezione catodica sui singoli elementi prima che questi vengano varati.

In casi particolari o in superfici verticali un’altra tecnica per il trattamento superficiale è la sabbiatura mediante acqua ad alta pressione, circa 400-500 Bar, e si arriva più o meno agli stessi risultati.

In Fig. 14, a destra, si vede la struttura come l'abbiamo trovata e come noi l'abbiamo resa ruvida per l'ancoraggio finale dell'overlay.

Fig. 15: ecco il famoso overlay. E' un prodotto che ha avuto tempi di sviluppo molto lunghi, sono 6 anni di studi che la Società americana ha impiegato a trovare un prodotto che oltre ad avere conducibilità limitata sembra aver risolto finalmente il problema meccanico, della resistenza di questi overlay. E' soltanto 1 cm di spessore sotto la rete. Sull'overlay poi si fanno le operazioni di impermeabilizzazione, se lo si crede.

I conci che alimentano sia l'armatura che la rete sono posti sotto il ponte e sono collegati ad una centralina (Fig. 16).

Il sistema di monitoraggio è estremamente complesso, le misure di potenziale della protezione catodica sono un po' più complesse di quella che è la sola lettura del potenziale. Bisogna fare alcune operazioni sulle quali credo non sia il caso di dilungarsi che giustificano comunque il fatto di avere un piccolo computer che rileva le misure, fa le operazioni che deve fare, le stampa, suona l'allarme, spegne gli alimentatori se c'è qualche problema ecc... Questo ponte è stato protetto con 25 Watt. La potenza maggiore consumata non era quella dell'alimentazione ma quella del raffreddamento degli alimentatori. Non mi soffermerei su quelli che sono i criteri di protezione perché forse sono un po' troppo specifici.

Vi ringrazio.

Fig. 1 - Ponte del viadotto Giaglione

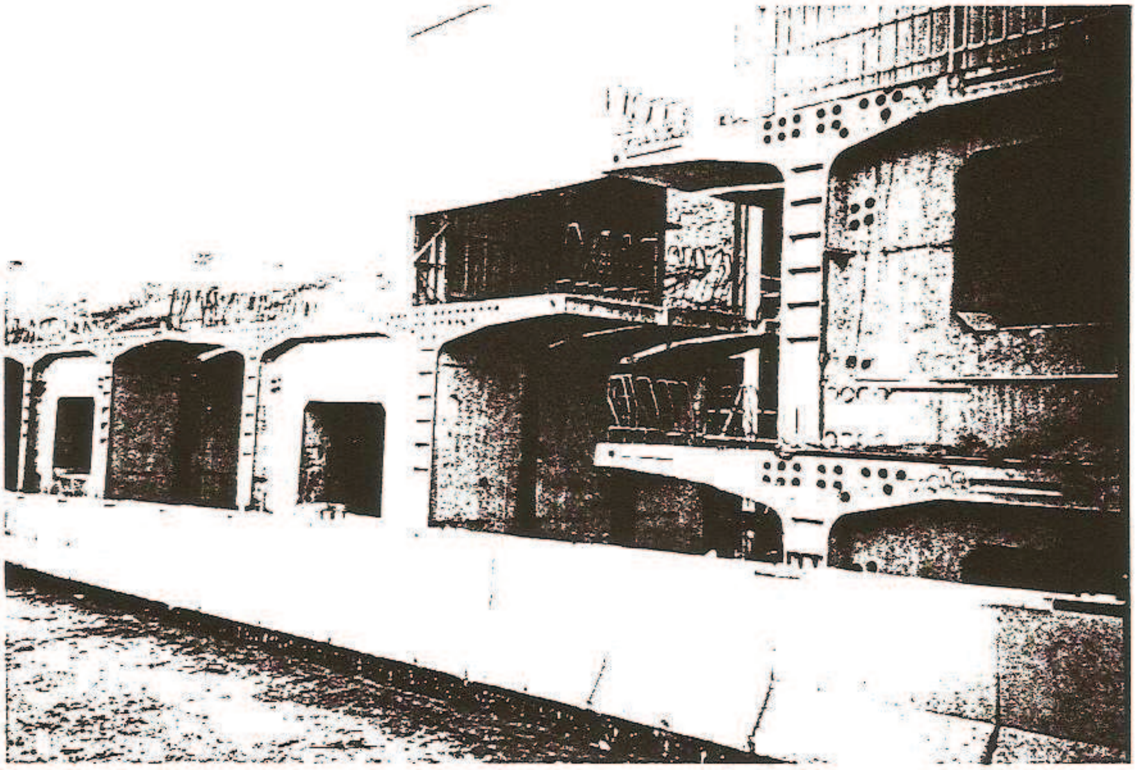


Fig. 2 - Conci del viadotto Clarea

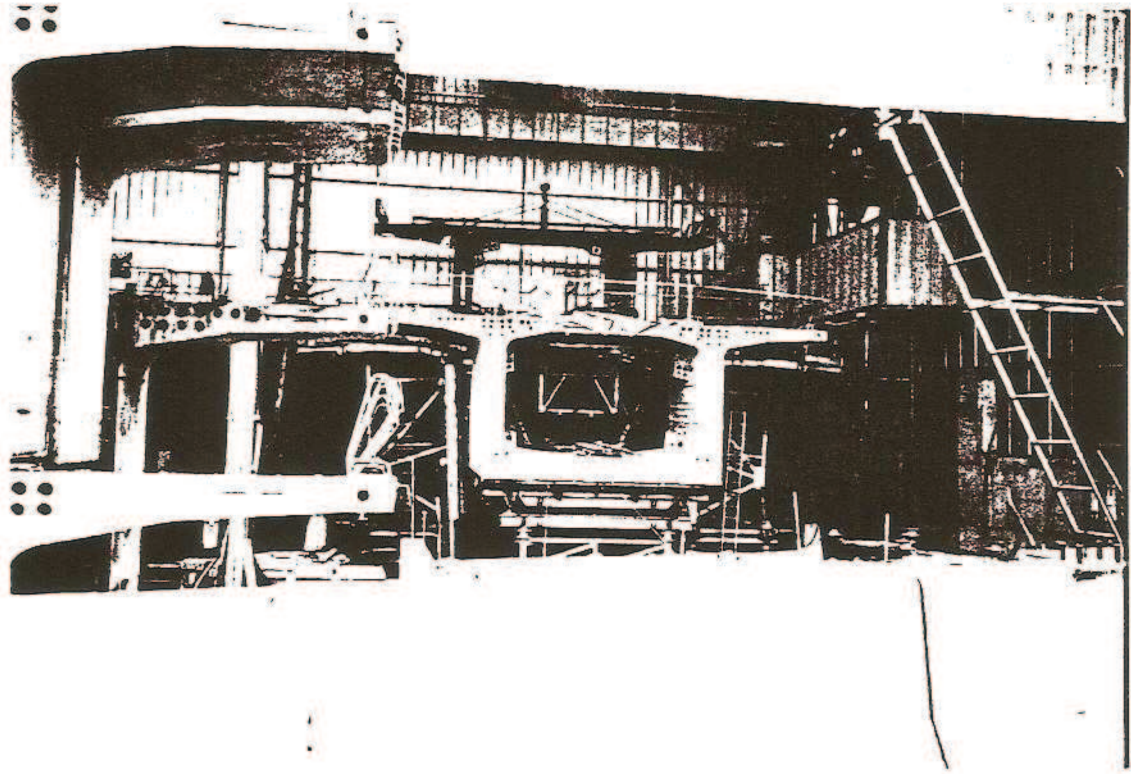


Fig. 3 - Area di prefabbricazione

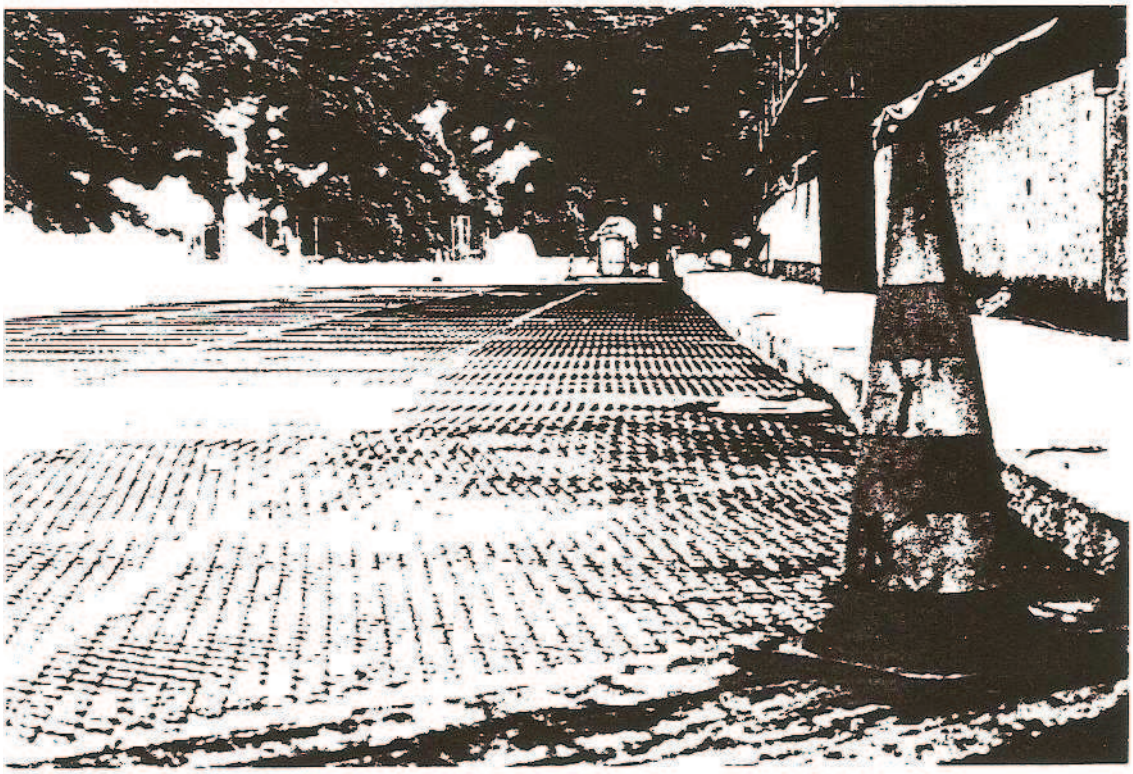


Fig. 4 - Installazione reti di titanio sul viadotto Giaglione

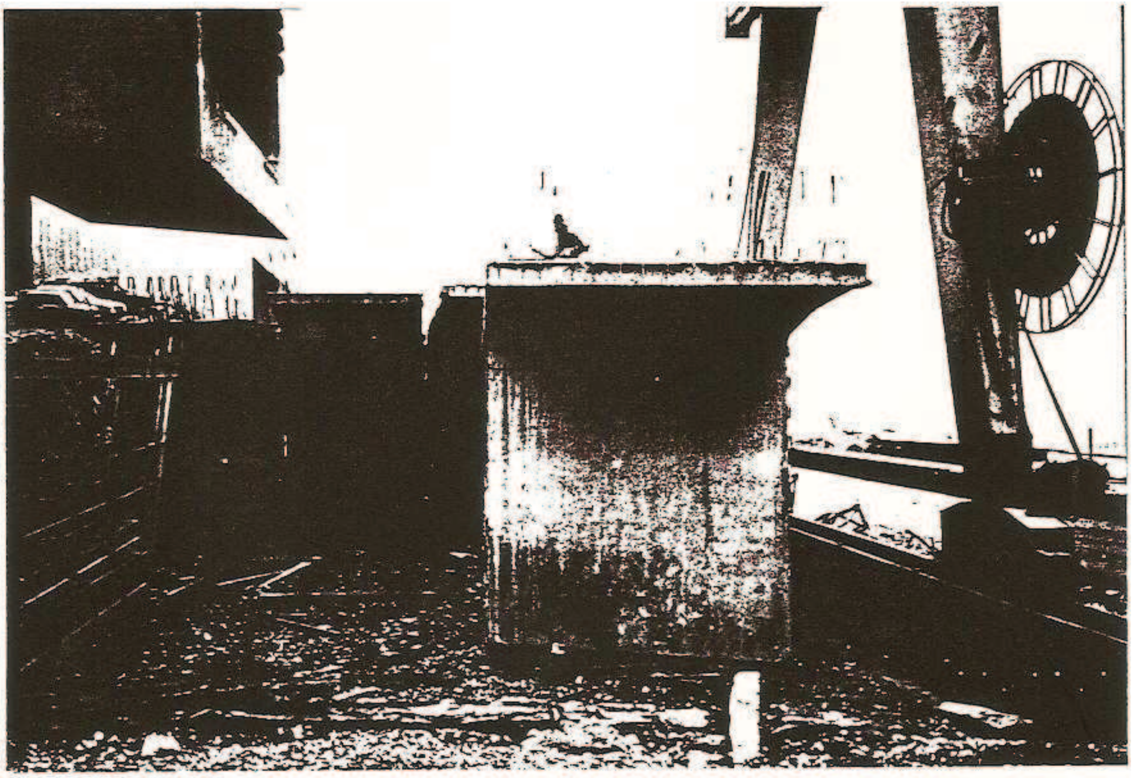
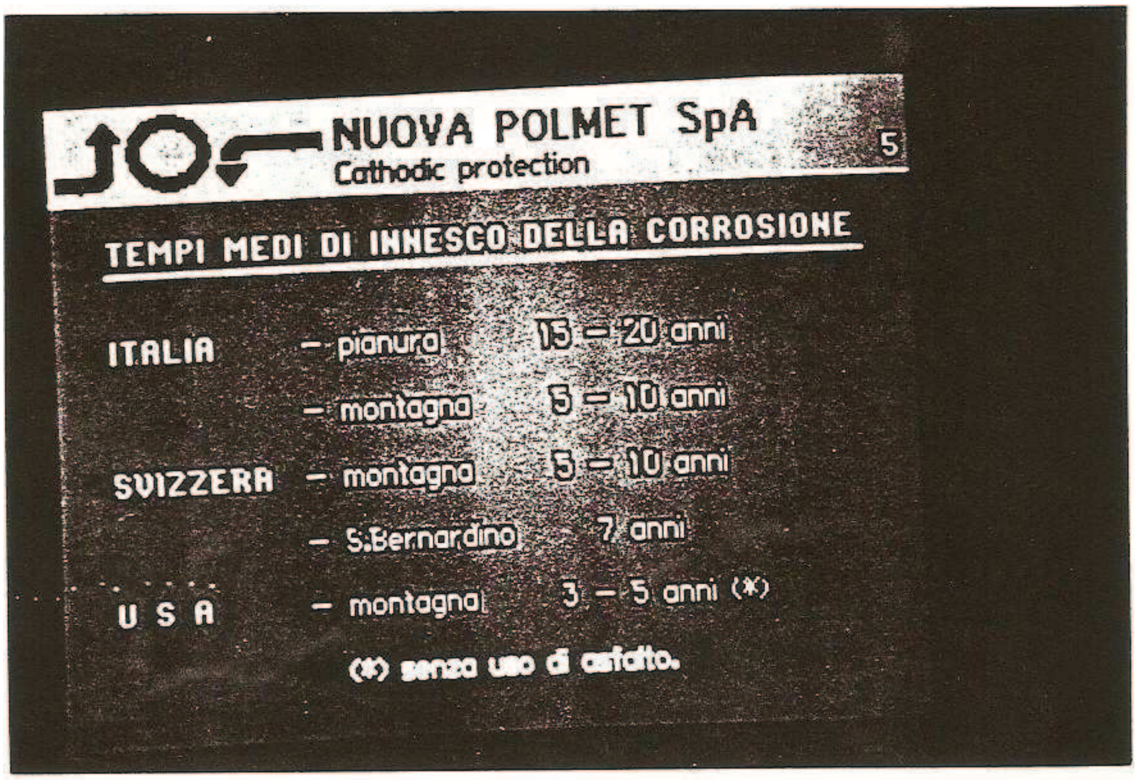


Fig. 5 - Movimentazione dei conci



NUOVA POLMET SpA
Cathodic protection
5

TEMPI MEDI DI INNESCO DELLA CORROSIONE

ITALIA	– pianura	15 – 20 anni
	– montagna	5 – 10 anni
SVIZZERA	– montagna	5 – 10 anni
	– S.Bernardino	7 anni
U S A	– montagna	3 – 5 anni (*)

(*) senza uso di asfalto.

Fig. 6 - Tempi medi di innesco corrosione

NUOVA POLMET SpA
cathodic protection

6

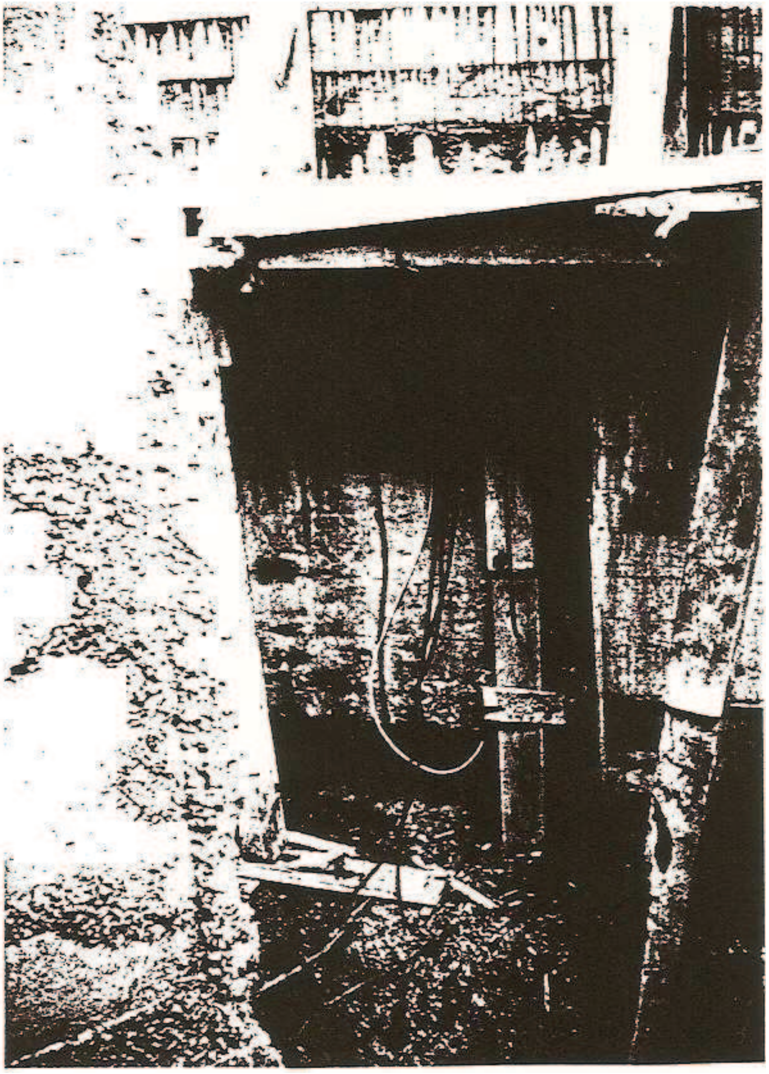
TECNICHE DI PREVENZIONE DELLA CORROSIONE

- inibitori di corrosione, es. $Ca(NO_2)_2$
- membrane impermeabili
- ferri rivestiti con resine epossidiche
- rapp. acqua/cemento molto basso e uso di riduttori di acqua
- miglioramento della compattezza del calcestruzzo
- protezione catodica

Fig. 7 - Tecniche di prevenzione della corrosione

Fig. 8 - Esempio di corrosione localizzata

Fig. 9 -
Cavi di collegamento degli elettrodi di riferimento



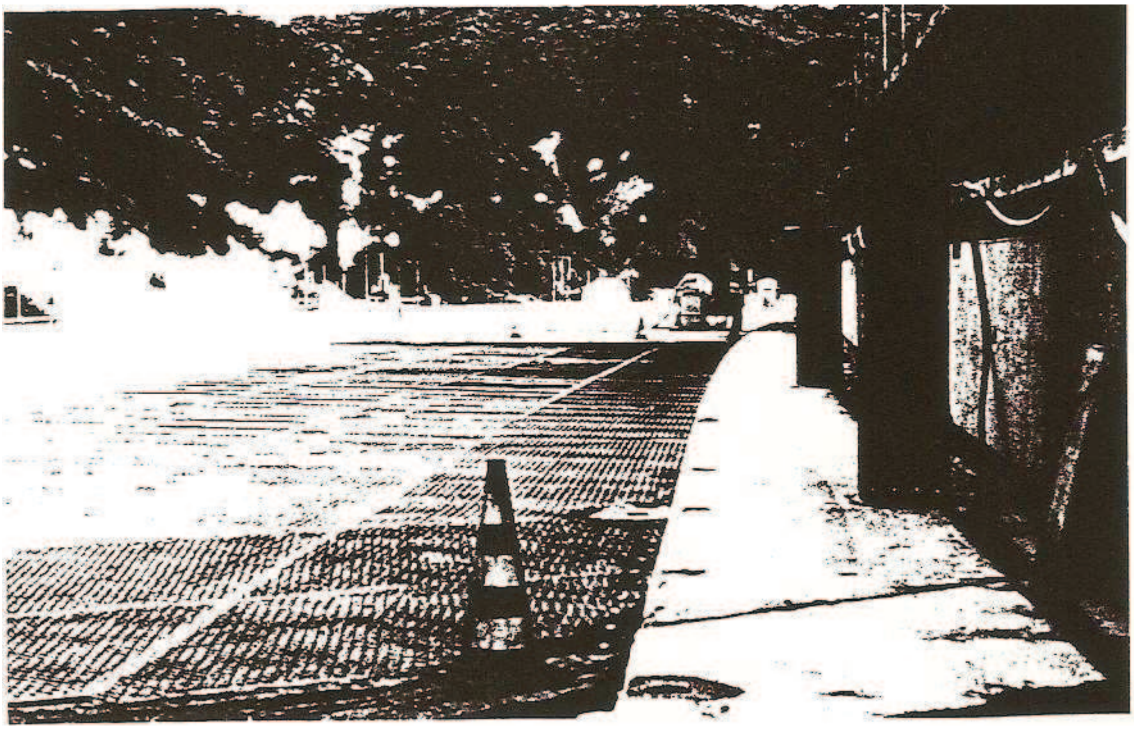


Fig. 10 - Sistemazione delle reti in titanio

Fig. 11 -
Saldatura della
piattina alla rete

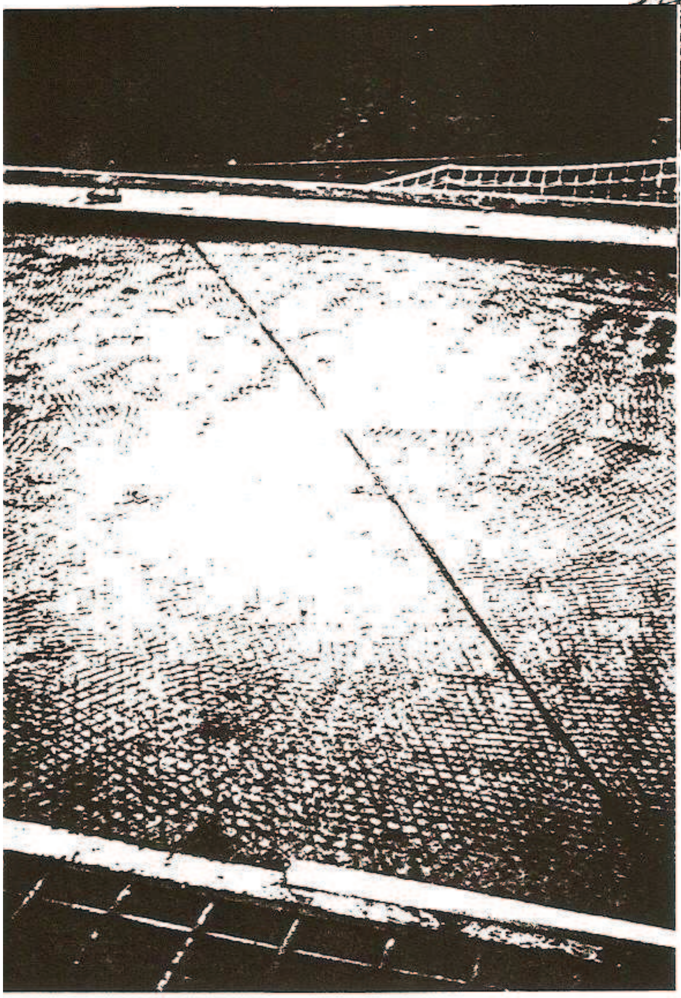


Fig. 12 -
Struttura in rete
di titanio ultimata

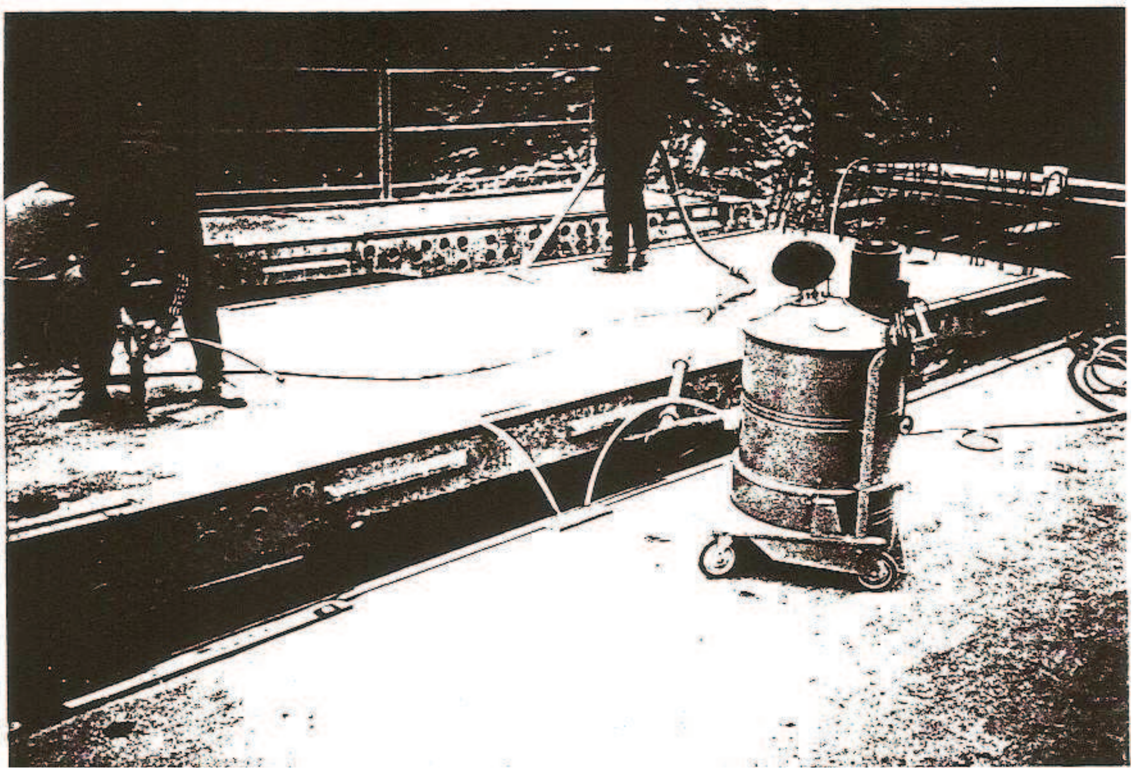


Fig. 13 - Operazione di pallinatura

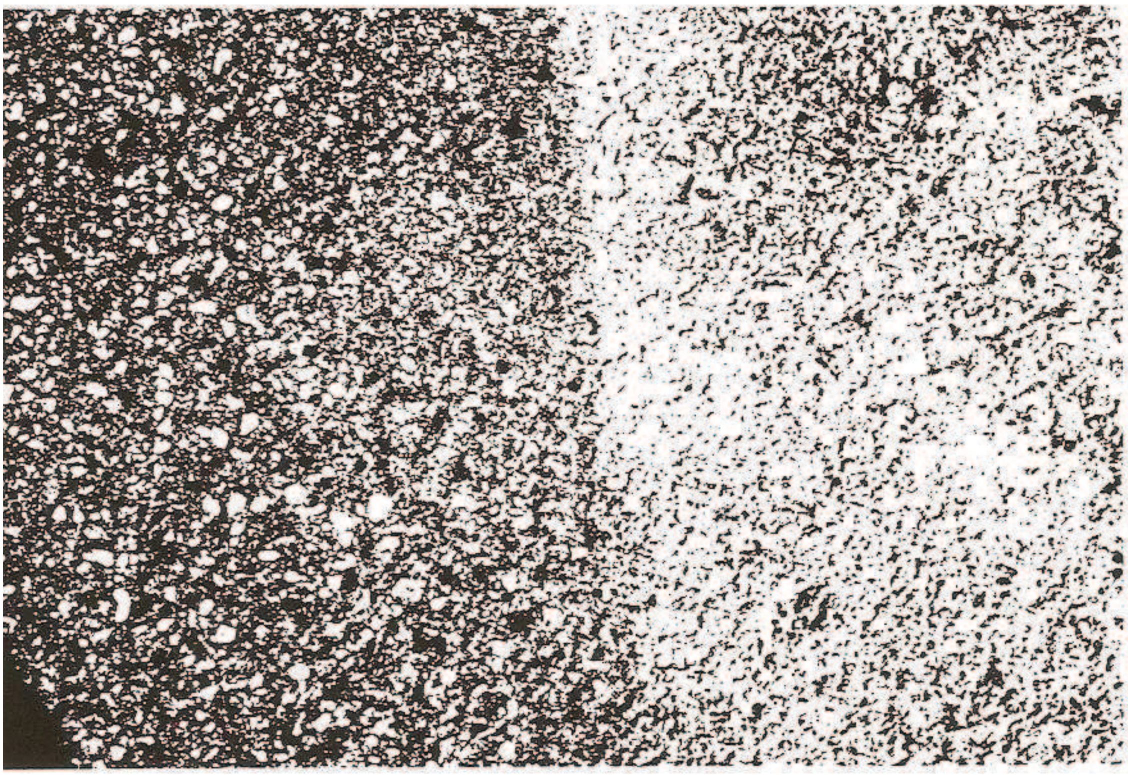


Fig. 14 - Confronto delle superfici prima e dopo il trattamento di pallinatura

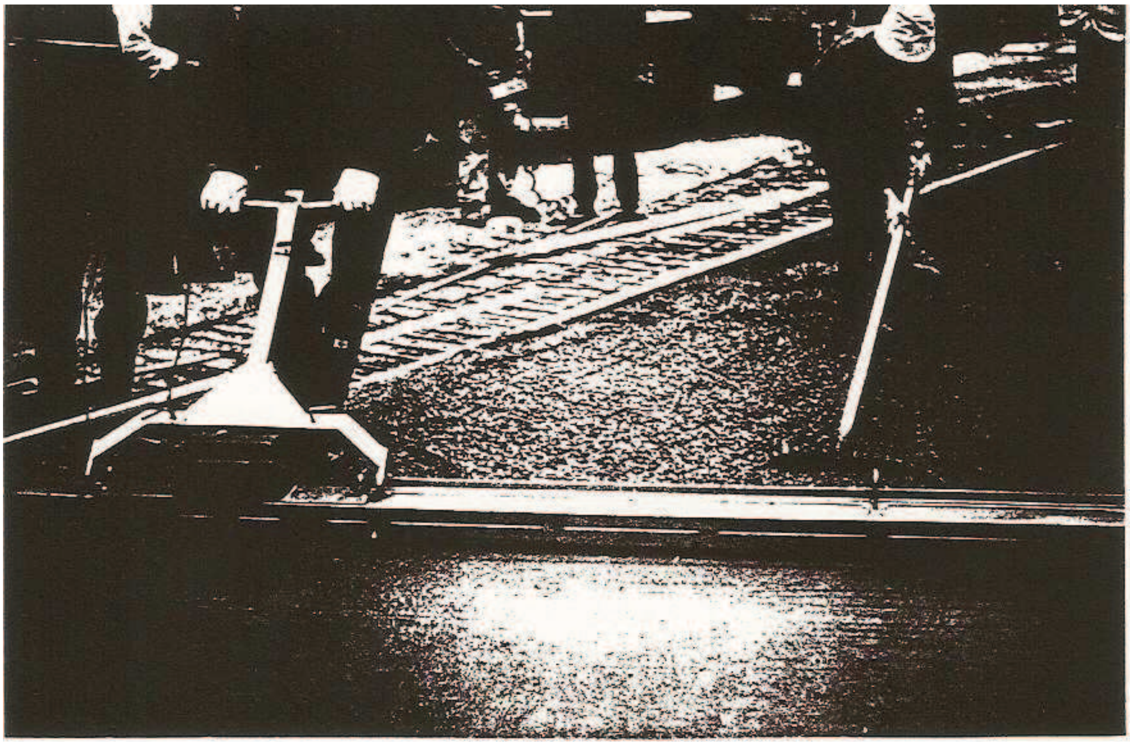


Fig. 15 - Messa in opera dell'"overlay"

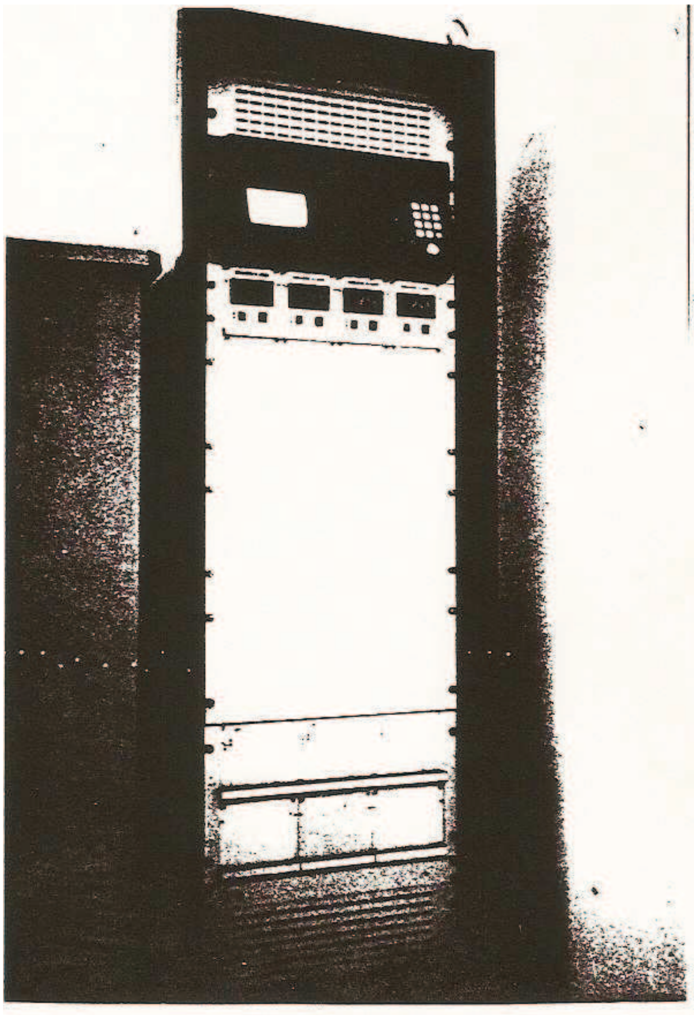


Fig. 16 - Centralina con sistema di monitoraggio

Ezio Debernardi
GTT

NUOVE APPLICAZIONI INDUSTRIALI DEL TITANIO

Signore e Signori buon pomeriggio, l’intervento che mi accingo a presentare può essere considerato un aggiornamento della panoramica sulle nuove applicazioni del titanio e sue leghe che vi presentai lo scorso anno.
Infatti in quest’ultimo anno abbiamo continuato con successo la nostra analisi degli impieghi del titanio in settori definiti "nuovi" poiché esulano dagli impieghi tradizionali, quali l’aerospaziale o l’industria chimica di base.

Vorrei presentarVi in particolar modo due cooperazioni con altrettante industrie private che hanno portato alla realizzazione di prototipi in leghe di titanio.

Il primo è stato realizzato nel settore della robotica industriale: una pinza di un robot di saldatura, montata su una linea per assemblaggio di scocche auto, che creava seri problemi al gruppo di motorizzazione (Figg. 1, 2, 3).

Nonostante fosse stata realizzata mediante una fusione di Alluminio, date le dimensioni rilevanti (lunghezza dei bracci 800 mm), il peso complessivo di 75 kg risultava essere troppo oneroso per un corretto funzionamento dell'attrezzatura.
Abbiamo realizzato in cooperazione con la Soc. Gerbi, leader nella produzione di pinze per saldatura, una struttura in lega di titanio (Ti 6Al-4V) estremamente resistente e leggera (54 kg). Tale struttura è stata collaudata in modo molto severo; infatti è stata sottoposta a 100.000 cicli di chiusura-apertura con carichi sugli elettrodi esasperati (circa 370 kg). I risultati sono stati ottimi.

Su input della società IVECO, stiamo realizzando una serie prototipale di barre di torsione per veicoli medio-pesanti (Figg. 4,5).

In questo caso la problematica è piuttosto complessa, l'obiettivo principale è quello di ottenere una barra di torsione che a parità di prestazioni sia molto più corta di quelle di serie. Quindi serve un materiale che pur presentando delle eccezionali caratteristiche meccaniche abbia un modulo elastico di gran lunga inferiore a quello degli acciai specifici. A questi requisiti rispondono pienamente le leghe β ed in particolare la β-C (Ti 3Al-8V-6Cr-4Mo-4Zr) che ha un modulo elastico pari a 9,65 x 10^4MPa, meno della metà di quello degli acciai.
Questo materiale, oltre alle elevate caratteristiche meccaniche (1240 MPa carico di rottura), presenta una elevata resistenza alla stress corrosion, anche in ambienti fortemente riducenti. Per queste ragioni sta trovando impiego in moltissime applicazioni: dalle teste di trivellazioni degli off-shores alla geotermia.

Credo che meriti una particolare attenzione e considerazione il vasto utilizzo che si fa del titanio come materiale da costruzione in Giappone.
L'anno scorso avevamo già accennato a questo impiego del titanio, tra poco avremo il piacere di ascoltare i tecnici della Sovrintendenza ai Beni Culturali di Roma che ci descriveranno che cosa si è realizzato nel settore del restauro dei monumenti lapidei in Italia, ma adesso Vi vorrei presentare alcuni esempi di applicazioni nel settore dell'edilizia (Figg. 6,7,8,9).

I primi casi di impiego nell'edilizia moderna risalgono al 1984, dal 1986 ad oggi sono stati realizzati più di 50 edifici facendo uso di svariate centinaia di tonnellate di titanio.

I Giapponesi considerano vincente l’impiego nelle coperture esterne soprattutto per le installazioni in riva al mare o nelle grandi città dove atmosfere corrosive provocano il veloce degrado di altri materiali metallici; non ultimo fattore di questo successo sembra essere stato il favore incontrato nel soddisfare il gusto e il senso estetico degli architetti.
La Fig. 10 mostra un operaio che sta effettuando la saldatura di alcune lamiere di copertura di un tetto con una saldatrice TIG portatile.

Se ancora ci fossero dubbi sulla difficoltà di assemblaggio e di messa in opera in cantiere di questo materiale, credo che questa testimonianza sia sufficiente a fugarli.

In conclusione si può affermare che le proiezioni negli impieghi "non tradizionali" del titanio fatte nel passato si stanno realizzando in misura ancora maggiore di quella preventivata e che questo metallo si sta affermando nel suo giusto ruolo di materiale strutturale.

La GTT dopo aver affinato il processo per la fabbricazione del metallo primario nel suo impianto di Santena (Fig. 11), mediante il processo elettrolitico (Fig. 12) in sali fusi, ha anche rivolto l’attenzione ai metodi ed alla metallurgia di fabbricazione delle leghe, in particolare quelle di ultima generazione.

E’ entrato in funzione alla fine dell’estate un impianto fusorio V.A.R. idoneo alla fabbricazione di quantitativi significativi di leghe sofisticate come le Beta, di leghe a memoria di forma (Ti-Ni), di materiali per superconduttori Ti-Nb e composti intermetallici come gli alluminiuri (Fig. 13). Questo sforzo è indirizzato ad utilizzare anche in Italia quelli che sono gli indirizzi della ricerca internazionale, per usi industriali.

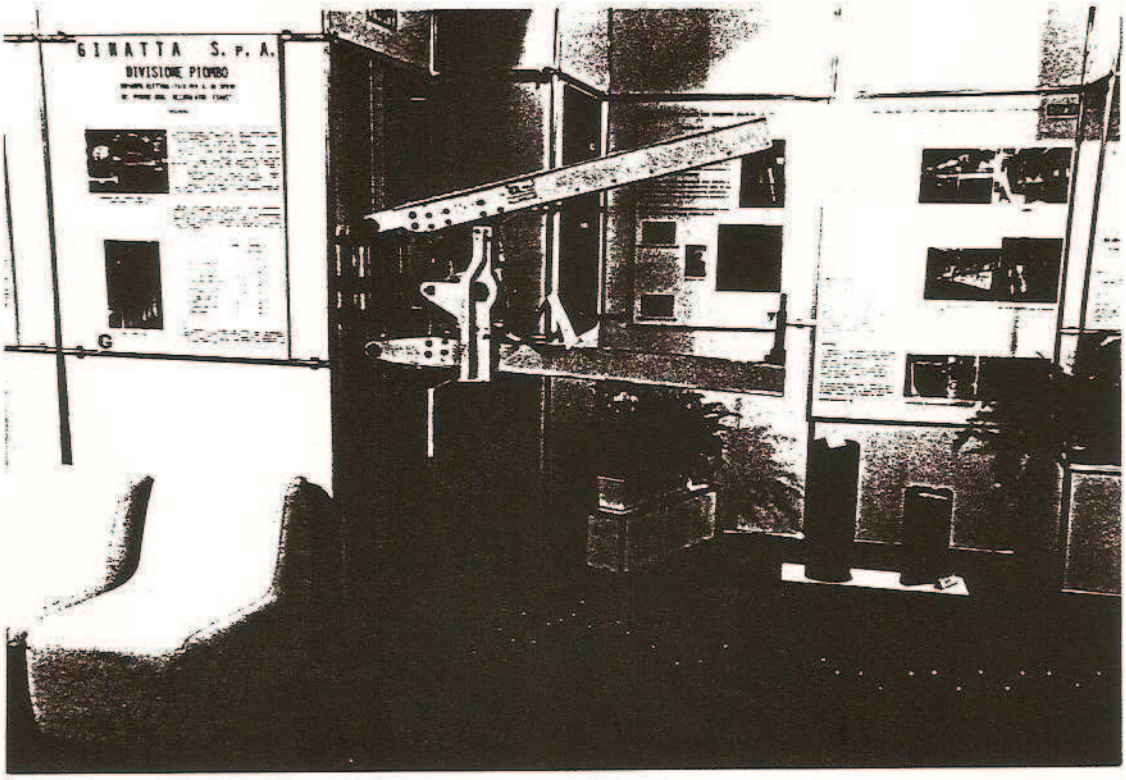


Fig. 1 - Pinza per robot di saldatura in lega di titanio Ti-6Al-4V

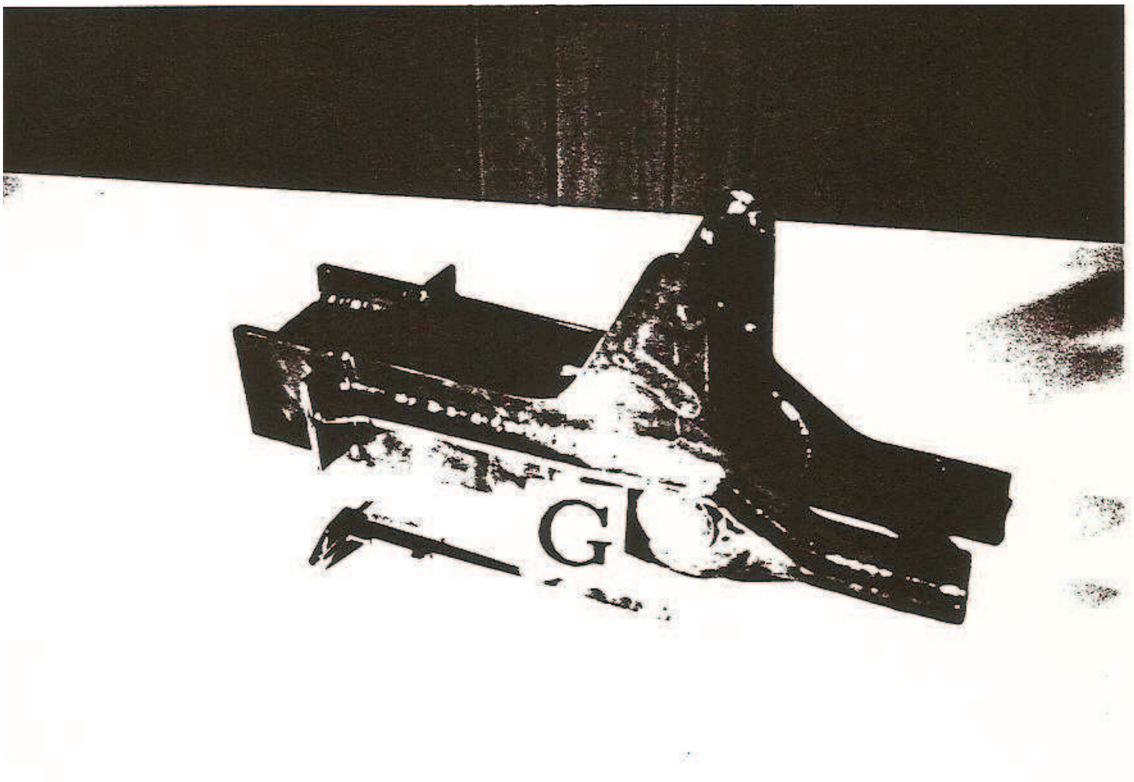


Fig. 2 - Particolare costruttivo della pinza per robot di saldatura

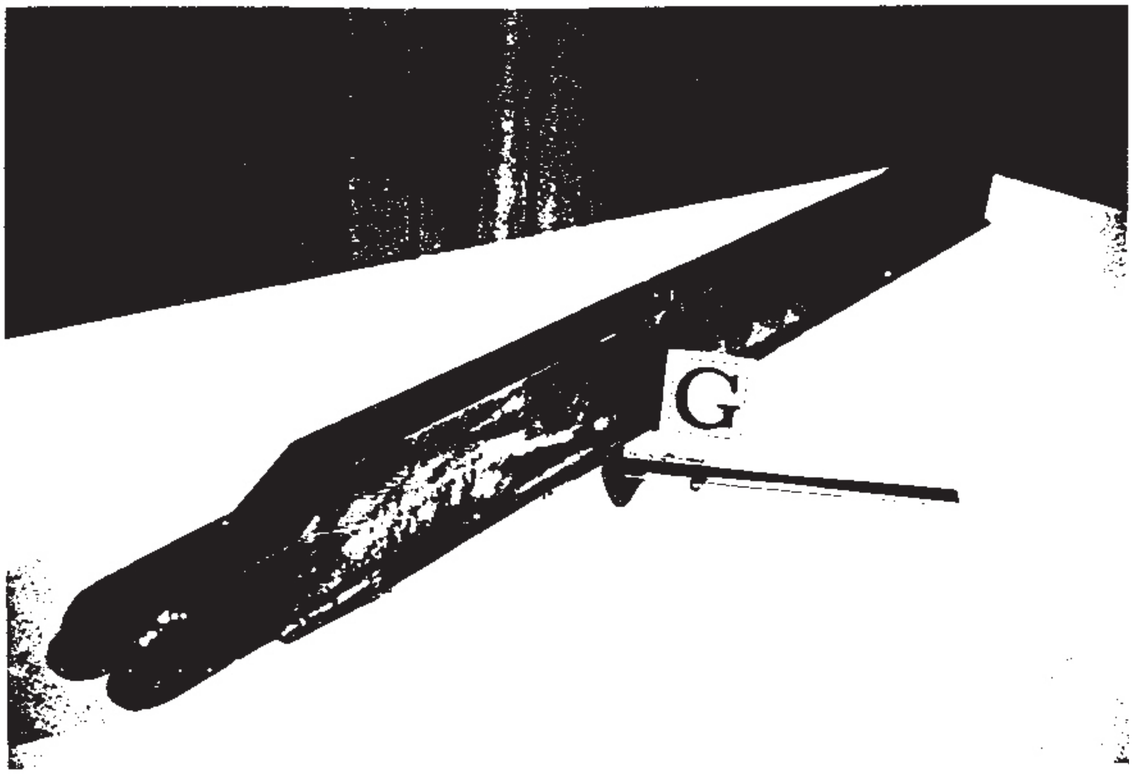


Fig. 3 - Particolare costruttivo della pinza per robot di saldatura

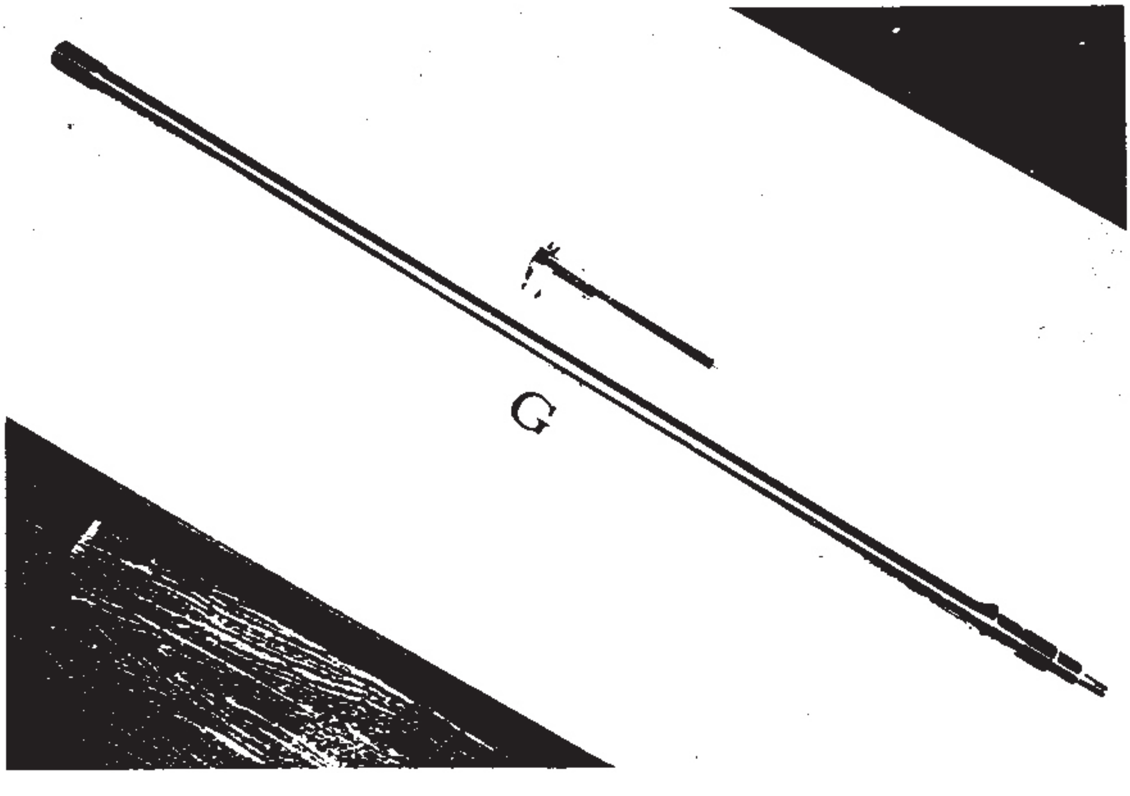


Fig. 4 - Barra di torsione per veicoli medio-pesanti IVECO, costruita in lega di titanio Beta-C

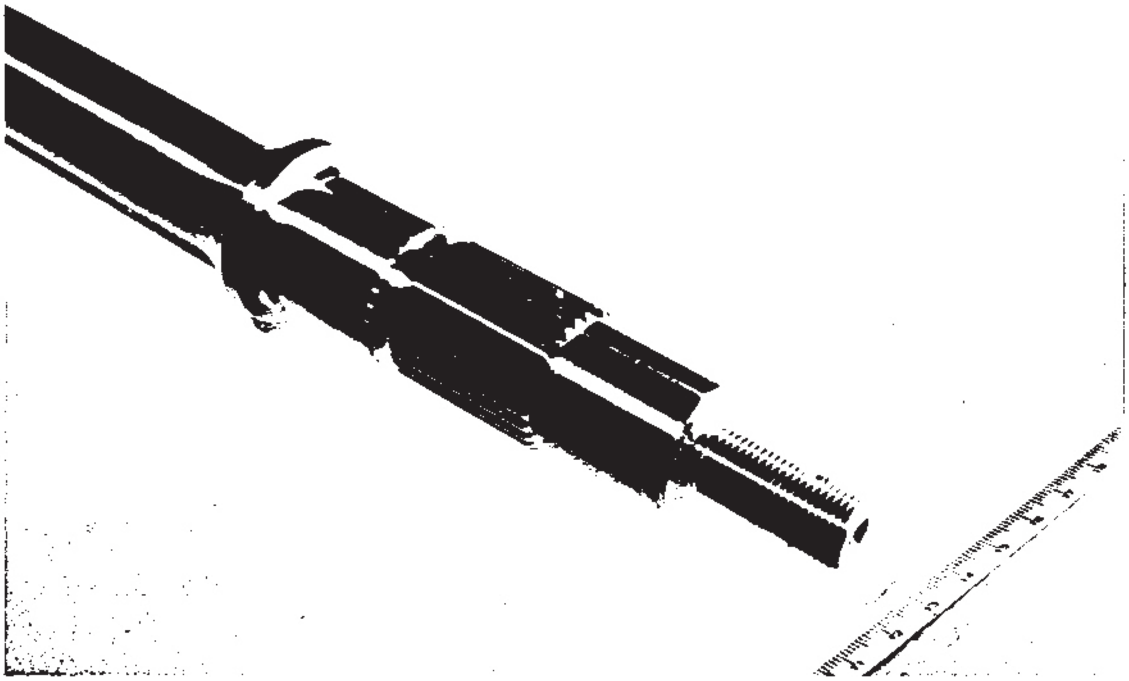


Fig. 5 - Particolare della barra di torsione in lega di titanio

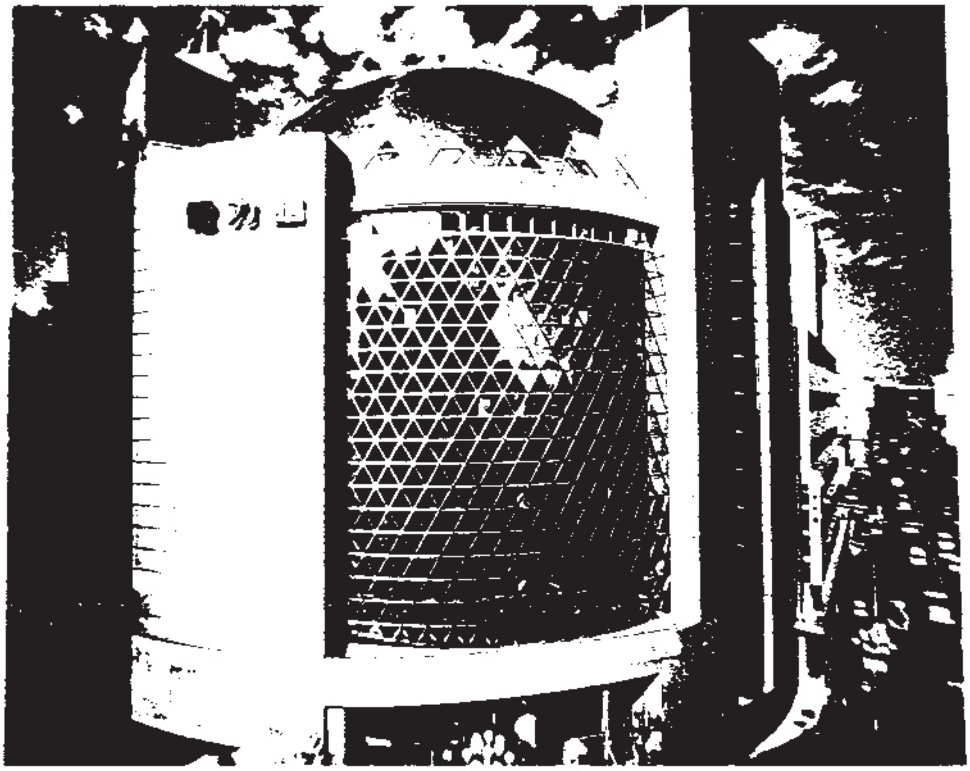


Fig. 6 - Applicazioni del titanio nell'edilizia giapponese. Tokyo, ufficio della Società per l'Energia Elettrica

Fig. 7 - Osaka, rivestimento esterno e pannelli

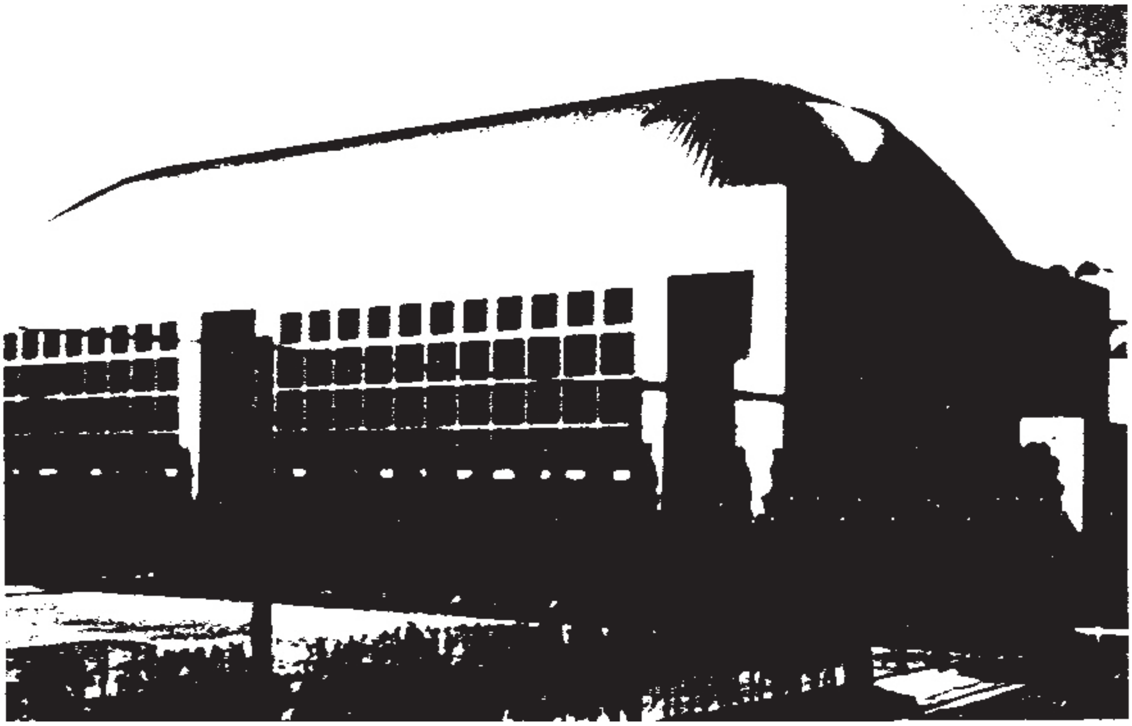


Fig. 8 - Yokohama University, tetto di 1000 m^2

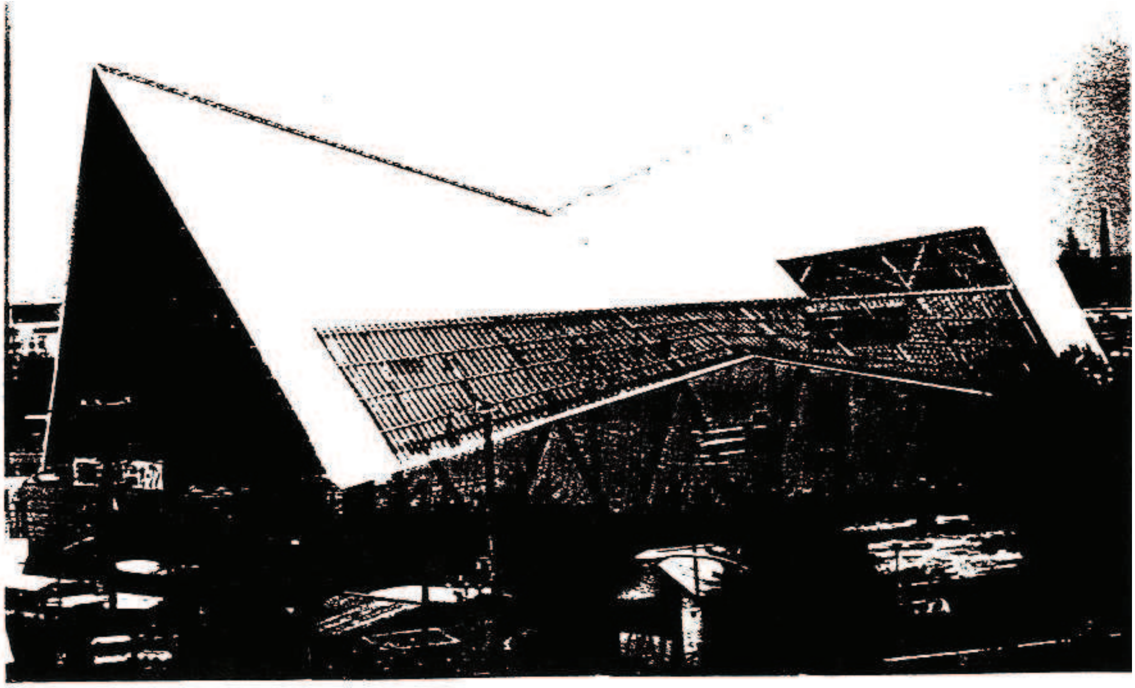


Fig. 9 - Acquario municipale Kobe

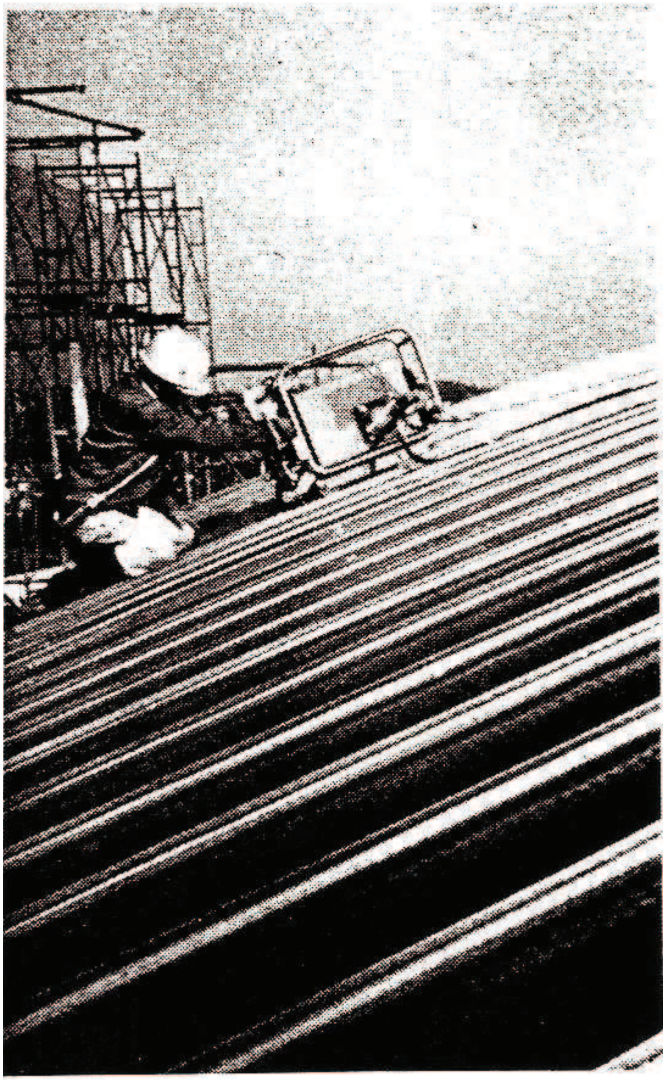


Fig. 10 - Saldatura in cantiere di lamiere in titanio su un tetto in Giappone

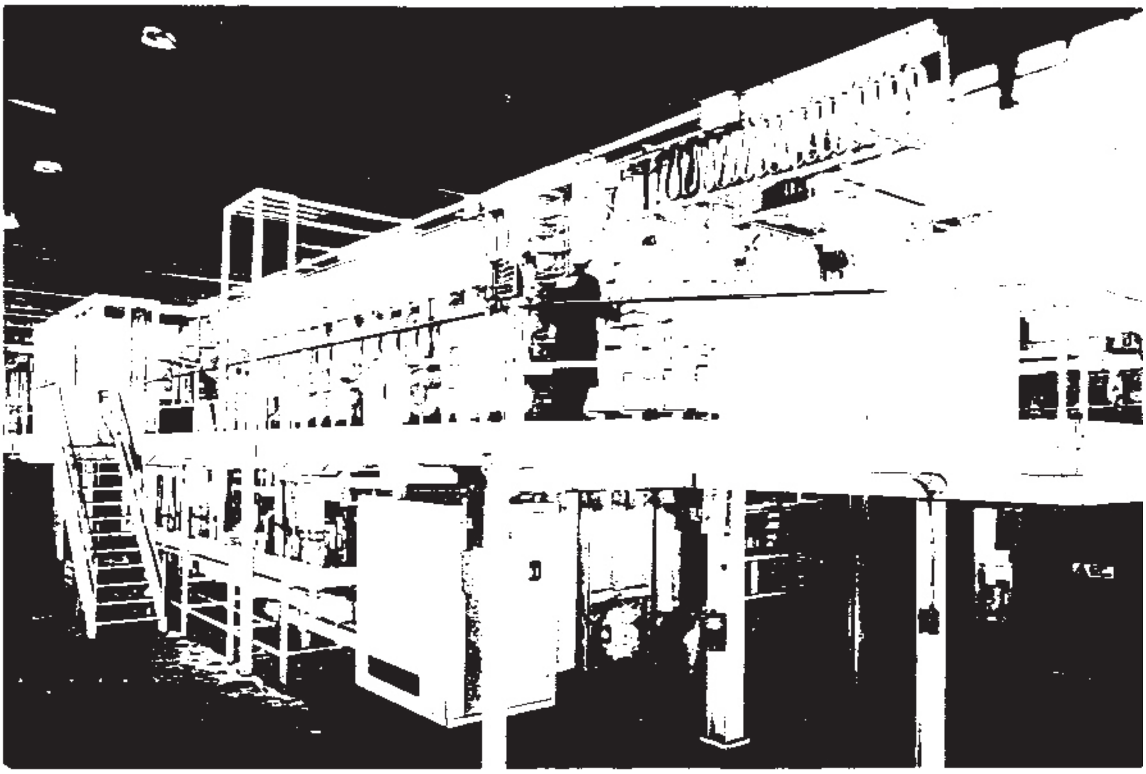


Fig. 11 - Impianti Modex III

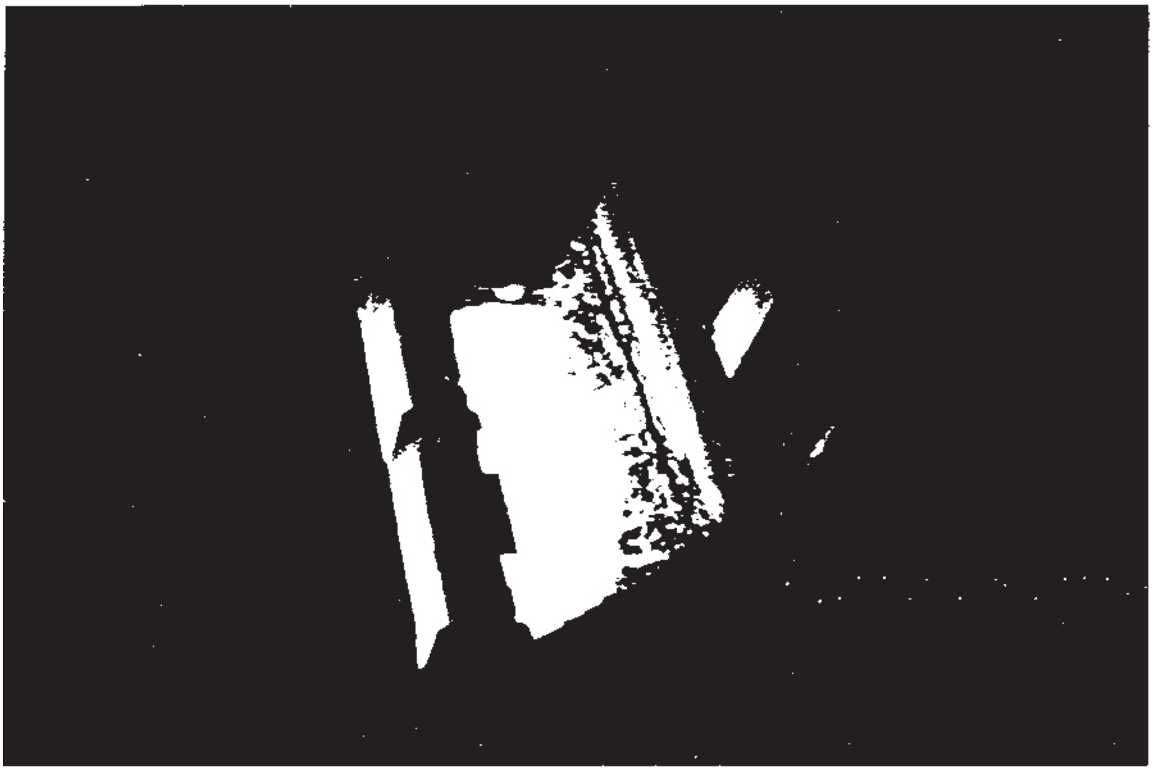


Fig. 12 - Estrazione di un catodo con dendriti

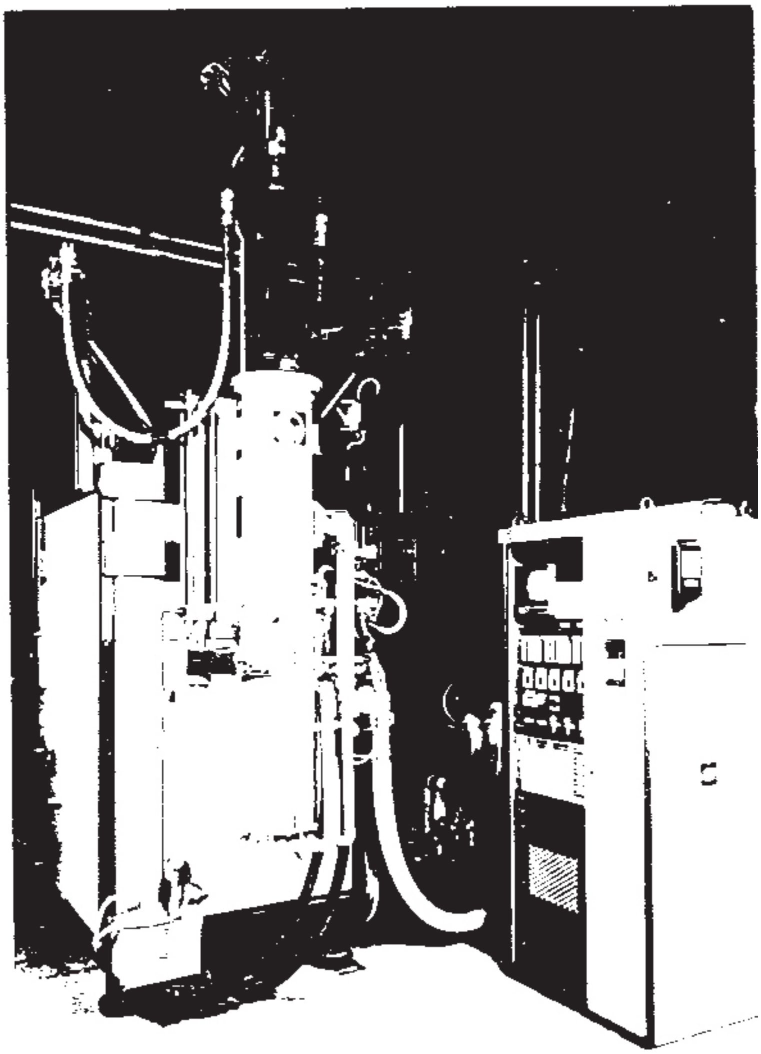


Fig. 13 - Forno V.A.R.

Ch. Sridhar Rao
Defence Metallurgical Research Laboratory, India

TITANIUM TECHNOLOGY AND ITS DEVELOPMENT IN INDIA

ABSTRACT

To meet the growing demand for titanium metal and its alloys in a variety of industries, including chemical, power generation, metallurgical etc., the metal industry has kept despite many ups and down, a steady growth in the annual capacity. Over the years, attempts have been made to reduce the product cost and increase the user acceptability. Increasing the production batchsize, reduction of process period, efficient management of energy and adoption of advance process control techniques, in addition to innovations on the basic process technology are some of the measures being pursued.

The paper reviews briefly the titanium in metal production technology. The development of titanium technology in India from the laboratory stage to the demonstration plant scale is discussed.

Coauthors
T.S. Sitaraman & RB Subramanyam, DMRL, India

1 - INTRODUCTION

Titanium metal industry is about 40 years old; and is limited to only few developed countries. During this period, due to fluctuating demand, the metal industry has faced many ups and downs yet maintained a progressive growth. In recent years, despite high cost of production, the demand for the metal has increased in a variety of industries, particularly chemical, power generation, electrochemical and metallurgical industries (1). It is also predicted that with the standardisation of new titanium alloy a period of fast growth will emerge and 21st century will see titanium as a major structural metal.

Extraction of titanium from its oxide minerals namely ilmenite (beneficiated ilmenite) and rutile through its intermediate product $TiC1_4$ is carried out by Kroll & Hunter processes. Although in their basic concept these metallothermic reduction process have not changed, marked progress on reduced cost of production, improved process and quality control techniques has however been made. From time to time attempts have also been made to develop fused salt electrolysis process to a commercially viable process. Recently Ginatta (2) are reported to have not only developed the process but also have set up plants for the commercial production of the metal.

India is fortunate to have large resources of titanium mainly in the form of ilmenite and rutile along its southern sea coast. Although titanium mineral production and processing industry is quite old in the country, there is no commercial production of titanium sponge. The technology for the large scale production of the metal from its chloride based on Kroll process has however been developed at the Defence Metallurgical Research Laboratory, Hyderabad and efforts to translate this into a commercial production unit are on hand.

The melting of titanium sponge and production of titanium seems like sheets, wires and forging is being carried out at the Mishra Dhatu Nigam Limited, (MIDHANI), Hyderabad having a capacity to produce about 200 TPY of titanium products. Midhani is also planning to set up facilities in collaboration with DMRL to produce titanium welded tubes. A number of companies in the country are also having facilities for the manufacture of a variety of titanium equipment.

The paper concerns the development of titanium metal production technology and its development in India and highlights the activities at DMRL on the production of titanium sponge.

2 - TITANIUM METAL PRODUCTION TECHNOLOGY

By far the two metallothermic reduction processes namely sodium (Hunter) and magnesium reduction (Kroll) processes are practiced for commercial production of titanium sponge.
The electrolytic process long ago predicted by W.J. Kroll as the technique which will ultimately be established for the production of titanium has also been developed. Recent reports indicate that this technique is also being adopted for the production of the metal.

The electrolytic process based on direct reduction of TiO_2 can offer many advantages. Despite many efforts to that end, it was realised that ductile metal could only be achieved through the chloride route. Hence all the electrolysis process so far developed are based on fused salt electrolysis of $TiCl_4$, There are however two distinct schools of development, one which adopts single (stage) cathode concept and the other adopts two cathode concept. It is known that $TiCl_4$ has poor solubility in chloride melt, unlike the lower chlorides which have good solubility in most alkali metal chloride baths. While the lower chlorides, and chlorine are highly corrosive chemicals the metal is very reactive and hence the development of electrolytic reduction of $TiCl_4$ had to meet many challenges:

1) Maintain adequate titanium spices in the melt.
2) Have suitable materials of construction and design to deposit the metal with least redissolution and corrosion problem.
3) Precise control of the reduction voltage to avoid co-deposition of the metals of carrier salts.
4) The use of suitable technique to recover the product with least wastage of carrier salts and the product metal.

Our experience (3) on the electrolysis process although limited, suggests that the process is simple for producing very good quality metal. However, engineering problems like corrosion harvesting of sponge without loss of quality and yield require detailing.

Sodium reduction process is practiced by three or four companies in the world. There are again two schools of development and practice; one adopting single stage reduction and the other two stage reduction. Chemical reduction of $TiCl_4$ with sodium is highly exothermic and to avoid freezing of NaCl (MP 810°C) or volatilisation of sodium (BP 880°C) a close control of temperature is required. The two stage reduction process perhaps facilitates the proper control of temperature and also the process can be carried out if not continuously at least in a semi-continuous fashion. Our own experience (4) with single stage reduction of $TiCl_4$ with sodium suggests that the process also is not difficult to operate. It generates very good quality crystalline metal. The overall yield of the good quality metal is crucial for the process.

Magnesium reduction process which is widely practiced the world over is perhaps the most accepted and yet the less expensive method of producing titanium sponge. The process offers many advantages especially the large productivity per unit and safety in handling and higher yield of high quality metal. There are certain practical differences in the methods adopted by various companies i.e.:

1) Mg reduction followed by vacuum distillation
2) Mg reduction followed by leaching
3) Mg reduction followed by inert gas sweep and leaching
4) Mg reduction and vacuum distillation in one assembly

These modification on the process as well as the innovations on the materials of construction, design of equipment and similar ones on recycle of magnesium and management of heat and material have contributed to greater success and acceptance of magnesium reduction process. The phenomenal rise in the production batch size of 10t has brought down the cost of production of the metal.

In India the magnesium reduction process has been studied in greater detail (5) and a demonstration plant of 100 tpy capacity has recently been set up at the Defence Metallurgical Research Laboratory, Hyderabad. The plant and the other one for the recovery of magnesium from $MgCl_2$ are in operation at DMRL.

During the last four decade titanium process industry has made remarkable progress. We see from the world titanium scene that the developments have distinctly been in the following directions:

1) Persistant efforts to establish the electrolytic process.
2) Reduce the product cost either by the electrolysis process or by modified magnesiothermic reduction process (to reduce process time, energy inputs and precise control of process).

3) Improve the quality of metal by increasing batch size and also by close control of process conditions.

4) Find newer applications for:
   a) the high quality metal (like superconductors, semi conductor)
   b) commercial alloy (like Ti alloys) and
   c) off grade metal (like addition in steels).

3 - INDIAN SCENE

The main constituents of the titanium industry in the country are mining, processing of titanium minerals, beneficiation of ilmenite, pigment oxide production, production of titanium semis and equipment. The Figure 1 shows the structure of titanium industry in the country, the names of the agencies and scale of operations involved. Mining and processing of minerals commenced in the second decade of this century followed by production of TiO_2 pigment by the sulphate route in the 50's. Production of titanium and titanium alloy semis and fabricated components like insoluble anodes for alkali industry, heat exchangers etc. commenced about a decade ago. In recent years, plants for the production of beneficiated ilmenite and pigment oxide by chloride route have come into operation.

It may be seen from the figure that production of titanium sponge on commercial scale is yet to commence in the country. However, efforts have continued for the last two decades. Table 1 shows the mile stones in the development of titanium sponge production technology in the country. it may be seen that all the established routes on the production of titanium sponge have been studied on laboratory scale at Bhabha Atomic Research Centre (Department of Atomic Energy). Pilot plant scale operation have been carried out at the Nuclear Fuel Complex of

Department of Atomic Energy for a comparative study of sodium and magnesium reduction processes. As a consequence of this a demonstration plant has been set up at Defence Metallurgical Research Laboratory (DMRL).

It is hoped that based on the technology developed at DMRL a commercial plant of 1000 tpy capacity will be set up soon in the country.

4 - DMRL PRACTICE

The process flow sheet for the production of titanium sponge at DMRL is shown in Figure 2. It consists of mainly three wings, first purification of $TiCl_4$, second metal production-reduction vacuum distillation and the third sponge handling and metal harvesting.

Fig. 3 shows the purification bay. The raw chloride received in steel drums, is pressure transferred to storage tanks. The chloride is preheated and then passed through two packed columns one to separate dissolved gases and the other for the separation of high boiling components and solids.
The pure chloride vapour is condensed and collected and used for reduction.

Magnesium ingots are pickled for the separation of metal oxide layer. The metal is dried and transferred for reduction to the metal production bay.

Fig. 4 shows the reduction and vacuum distillation bay.
The reduction batch size is 2000 kg electric resistance furnaces are used both for reduction and vacuum distillation.

Fig. 5 shows the sponge harvesting bay. Horizontal and vertical hydraulic presses and jaw crushers are used to crush the sponge cake to 2-12mm size product. Table 2 shows the analysis of $TiCl_4$, Mg used and titanium sponge obtained.

At DMRL we are working simultaneously on two aspects i.e.:

1) use of computer based process control system
2) use of a combination unit

1) A Microprocessor based controller system has been procured and installed recently. it is proposed to operate the chloride purification, reduction and vacuum distillation facilities with the help of this controller. Efforts are being made to commission the unit along with the indegenously available process control field instruments.

2) By confining the reduction and vacuum distillation operation to one unit - called combination unit - many advantages like saving in process time, lesser energy input and improved quality of sponge are expected to be achieved. Fabrication of a furnace and the process equipment for this purpose have been taken up. Plans are on hand to commission this unit.

5 - SUMMARY

India is rich in titanium resources and there exists a basic industry for processing titanium minerals for the production of titanium tetrachloride, titanium and titanium alloy products. Efforts to establish a commercial plant for the production of titanium sponge based on the technology developed at DMRL are being made.

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7 - ACKNOWLEDGEMENTS

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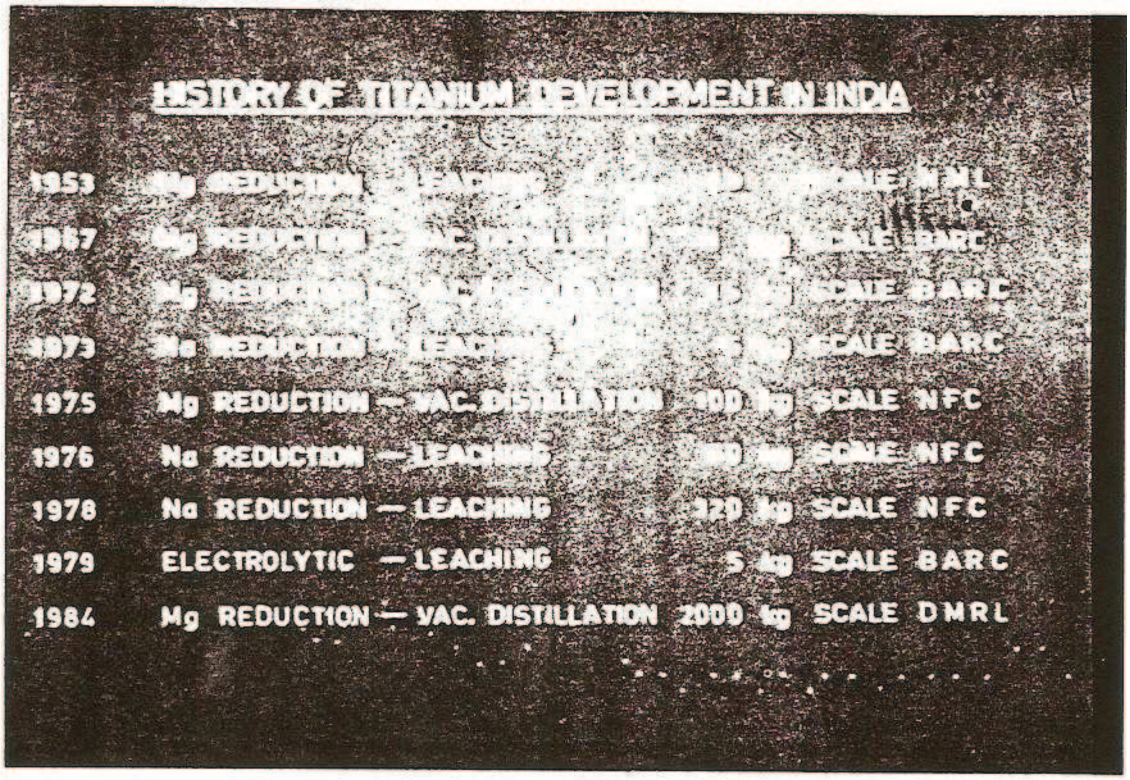
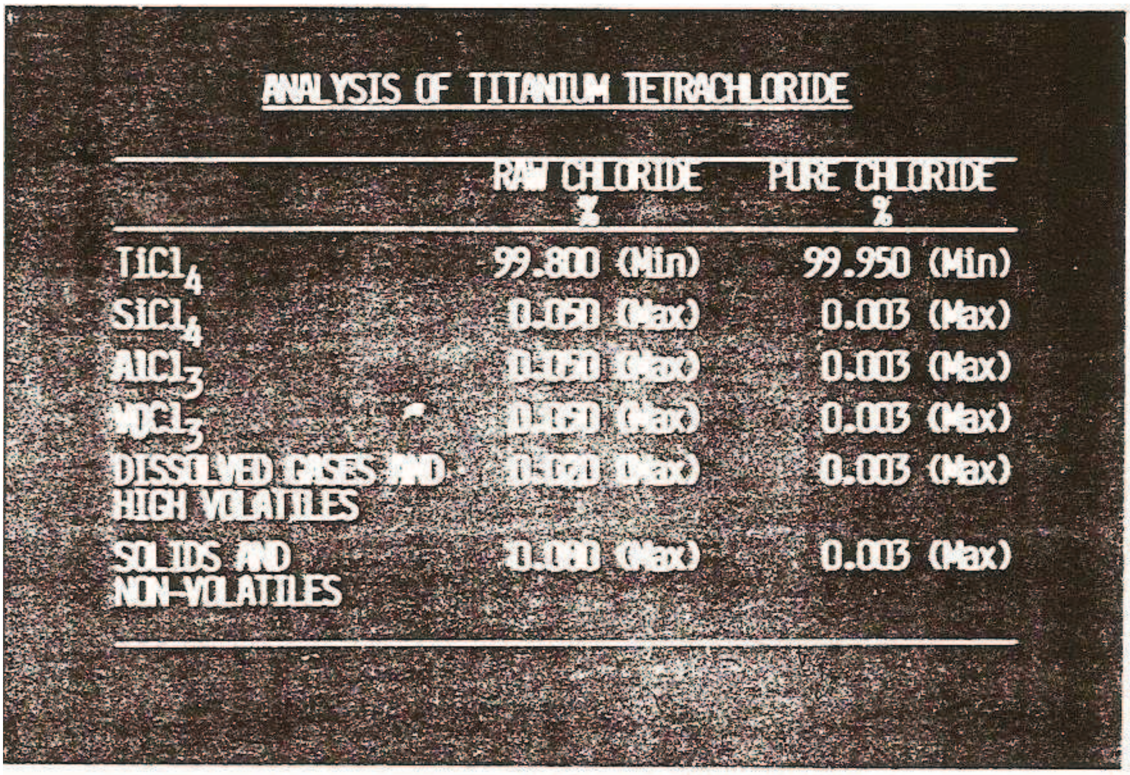


HISTORY OF TITANIUM DEVELOPMENT IN INDIA

1953	Mg REDUCTION — LEACHING	[illegible] kg SCALE	NML
1967	Mg REDUCTION — VAC. DISTILLATION	[illegible] kg SCALE	BARC
1972	Mg REDUCTION — VAC. DISTILLATION	[illegible] kg SCALE	BARC
1973	Na REDUCTION — LEACHING	5 kg SCALE	BARC
1975	Mg REDUCTION — VAC. DISTILLATION	100 kg SCALE	NFC
1976	Na REDUCTION — LEACHING	[illegible] kg SCALE	NFC
1978	Na REDUCTION — LEACHING	320 kg SCALE	NFC
1979	ELECTROLYTIC — LEACHING	5 kg SCALE	BARC
1984	Mg REDUCTION — VAC. DISTILLATION	2000 kg SCALE	DMRL

Table 1



ANALYSIS OF TITANIUM TETRACHLORIDE

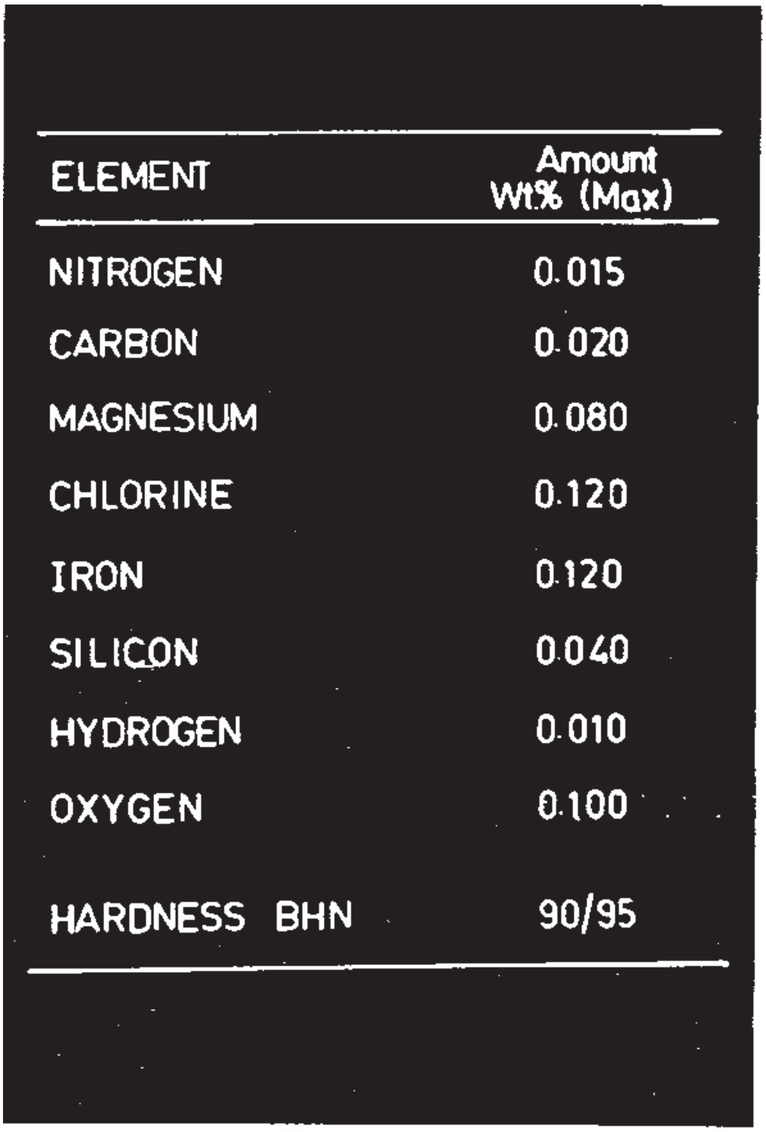
	RAW CHLORIDE %	PURE CHLORIDE %
$TiCl_4$	99.800 (Min)	99.950 (Min)
$SiCl_4$	0.050 (Max)	0.003 (Max)
$AlCl_3$	0.050 (Max)	0.003 (Max)
$VOCl_3$	0.050 (Max)	0.003 (Max)
DISSOLVED GASES AND HIGH VOLATILES	0.020 (Max)	0.003 (Max)
SOLIDS AND NON-VOLATILES	0.080 (Max)	0.003 (Max)

Table 2.1

ANALYSIS OF MAGNESIUM

ELEMENT	(PPM)
Aluminium	30
Iron	400
Silicon	50
Copper	40
Manganese	60
Tin	50
Magnesium (by difference)	> 99.9

Table 2.2



ELEMENT	Amount Wt% (Max)
NITROGEN	0.015
CARBON	0.020
MAGNESIUM	0.080
CHLORINE	0.120
IRON	0.120
SILICON	0.040
HYDROGEN	0.010
OXYGEN	0.100
HARDNESS BHN	90/95

Table 2.3

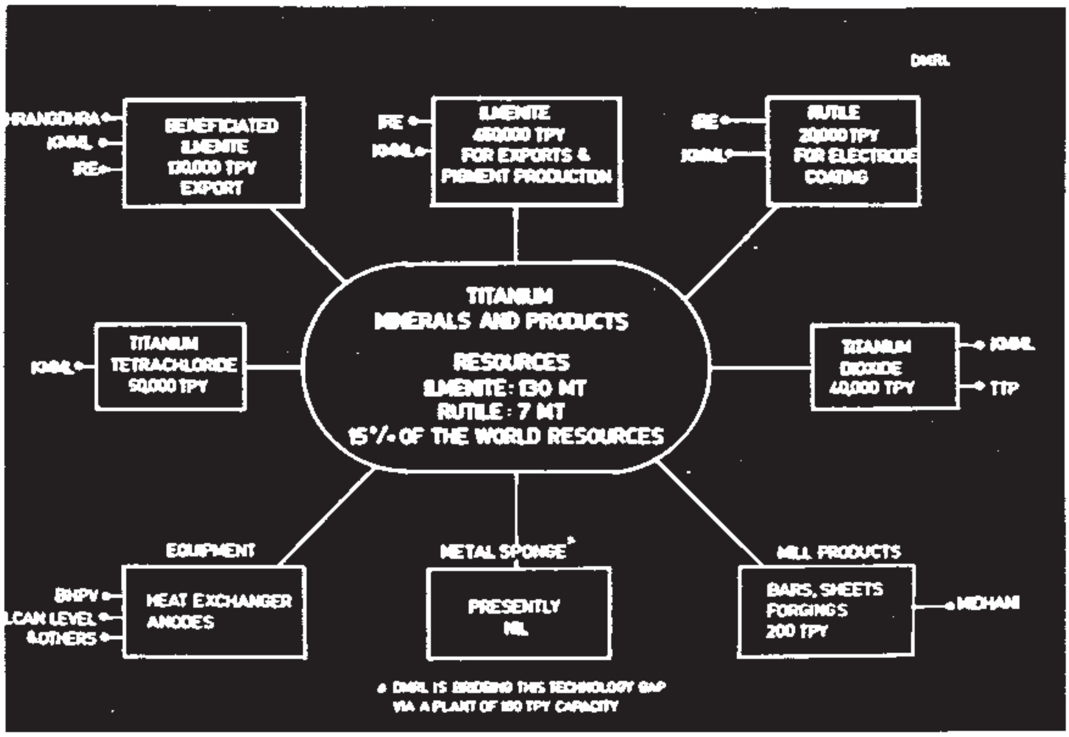

DMRL
HRANGDHRA
KMML
IRE
BENEFICIATED ILMENITE 130,000 TPY EXPORT
IRE
KMML
ILMENITE 480000 TPY FOR EXPORTS & PIGMENT PRODUCTION
IRE
KMML
RUTILE 20,000 TPY FOR ELECTRODE COATING
KMML
TITANIUM TETRACHLORIDE 50,000 TPY
TITANIUM MINERALS AND PRODUCTS
RESOURCES
ILMENITE : 130 MT
RUTILE : 7 MT
15% OF THE WORLD RESOURCES
TITANIUM DIOXIDE 40,000 TPY
KMML
TTP
EQUIPMENT
BHPV
LCAN LEVEL
& OTHERS
HEAT EXCHANGER ANODES
METAL SPONGE*
PRESENTLY NIL
MILL PRODUCTS
BARS, SHEETS FORGINGS 200 TPY
MIDHANI
* DMRL IS BRIDGING THIS TECHNOLOGY GAP VIA A PLANT OF 100 TPY CAPACITY

Fig. 1

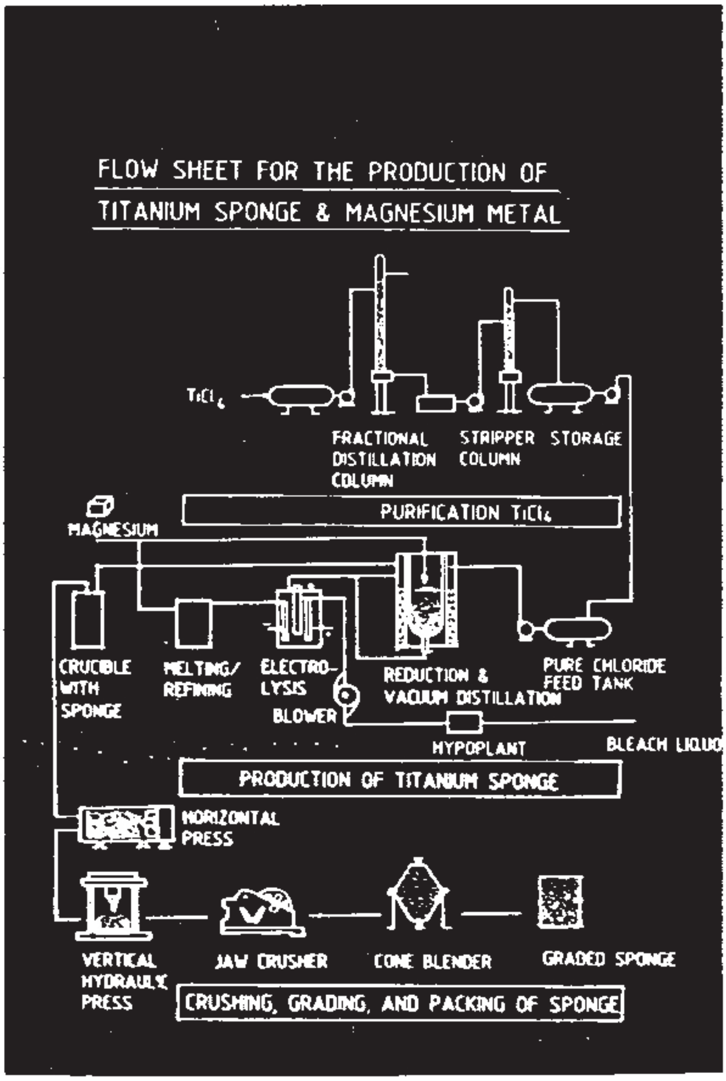

FLOW SHEET FOR THE PRODUCTION OF
TITANIUM SPONGE & MAGNESIUM METAL
TiCl₄
FRACTIONAL DISTILLATION COLUMN
STRIPPER COLUMN
STORAGE
PURIFICATION TiCl₄
MAGNESIUM
CRUCIBLE WITH SPONGE
MELTING/ REFINING
ELECTRO-LYSIS
BLOWER
REDUCTION & VACUUM DISTILLATION
PURE CHLORIDE FEED TANK
HYPOPLANT
BLEACH LIQUO
PRODUCTION OF TITANIUM SPONGE
HORIZONTAL PRESS
VERTICAL HYDRAULIC PRESS
JAW CRUSHER
CONE BLENDER
GRADED SPONGE
CRUSHING, GRADING, AND PACKING OF SPONGE

Fig. 2

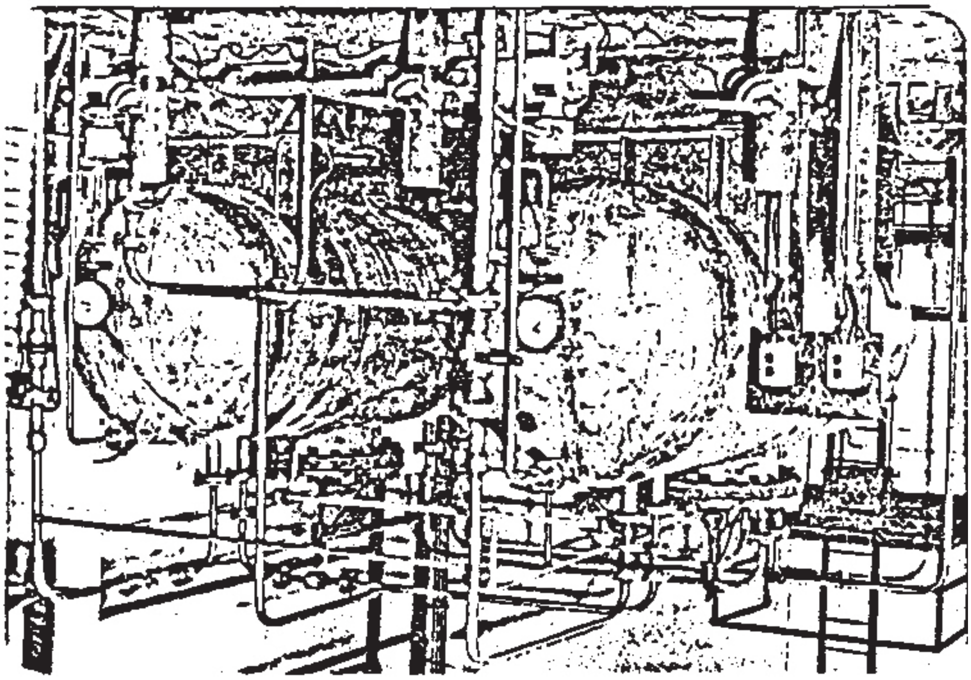


Fig. 3 - Purification bay

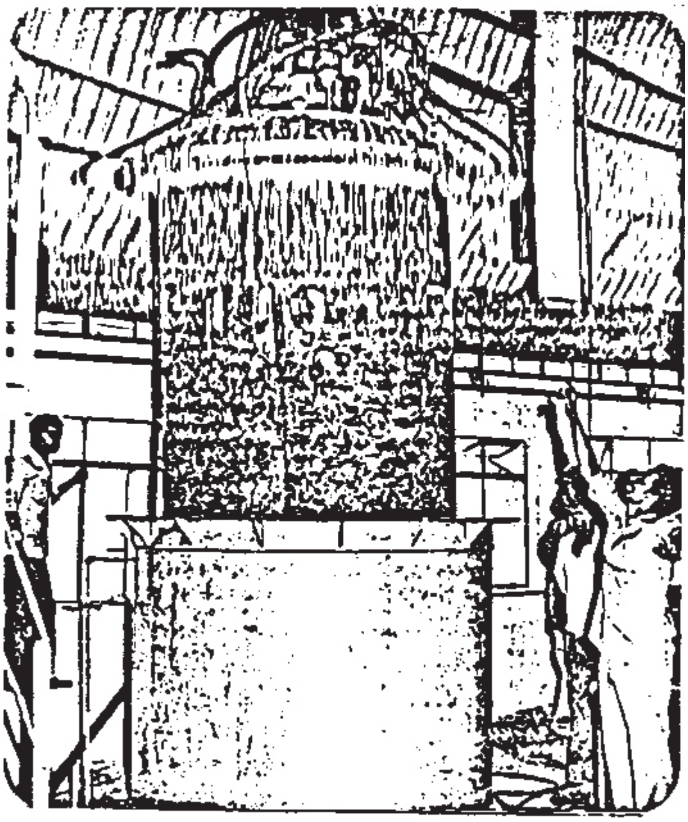


Fig. 4 - Reduction bay

Fig. 5 - Vertical hydraulic presses

J. Schmuck
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SURFACE PROPERTIES ENHANCEMENTS OF Ti6Al4V PARTS FOR MECHANICAL APPLICATIONS

1 - INTRODUCTION

Titanium alloys are widely used in aeronautics because of their low specific weight and their good fatigue properties and in chemical industries because of their good corrosion resistance. Their application in Mechanical Engineering is however hampered by their "poor" scuffing resistance.

An evaluation of the scuffing resistance of the Ti-6Al-4V alloy under pure sliding, pure rolling and combined rolling and sliding conditions, performed for representative loads and speeds, is presented in this paper. A dual approach is used. The materials is first tested as a structural alloy, to examine its "volume" properties as a lubricated gear or roller bearing material. Sliding is introduced in the same tests. The material is then tested under dry friction in a fretting rig. Finally, results with coatings like plasma sprayed carbides and oxides or nitrides obtained by plasma nitriding are presented through their effects on both fatigue life and scuffing.

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2 - TITANIUM ALLOY IN LUBRICATED HERTZIAN (EHD) CONTACTS

2.1 - Generalities

Hertzian contacts are found in ball, roller bearings, cams and gears. These mechanisms are characterised by high contact pressures (> 1GPa) and both rolling and sliding conditions. In most applications, the elastohydrodynamic (EHD) film thickness is of the same order of magnitude as the roughness of the working surfaces (RMS ≈ 0,5 µm). Thus the material used must withstand:

- High contact pressures and thus have high "volume" or bulk resistance.
- sliding velocities and thus have high "surface" resistance.

An evaluation of the performance of titanium alloys as a candidate for such applications must therefore address both "volume" and "surface" aspects of the problem.

2.2 - Volume aspects

The volume aspects will be studied in a high precision disk machine by imposing high contact pressure between two specimens, operating under pure rolling conditions, and separated by a thick elastohydrodynamic film. This is achieved with a high viscosity oil.

2.3 - Surface aspects

Surface resistance will be assessed in two ways:

- under pure rolling conditions but with surface interactions. This is achieved with a low viscosity oil,
- under combined rolling and sliding conditions.

In all volume and surface tests:

- the total rolling velocity ($U_1 + U_2$) is kept constant (Table 1)
- all specimens are identical
- the slide/roll ratio $(U_1 - U_2)/(U_1 + U_2)$ is constant in all sliding tests.

Particulars are given in Table 1.

2.4 - Simulation conditions and disk machine

The running conditions (Table 1) retained for this test are representative of those found in gear for aeronautical applications. Simulation is based on the faithful reproduction of the contact conditions (load, pressure and speed) and materials (base materials, lubricant, atmosphere ...) prevalent at a particular point of the gear profile (Fig. 1). A schematic view of the disc machine is also given in figure 1. It consists of two high speed electric motors mounted on a heavy stand. Tests specimens are fastened directly on each shaft. The first motor is fixed, the second is supported on two hydrostatic bearings and has two degrees of freedom, one to accommodate specimens of different diameters (I) and the other for measure friction (II).

The characteristics of this high precision, high speed machine are given in Table 1.

2.5 - Results

Uncoated Titanium

Various tests were conducted for three parameter combinations (normal load, slide/roll ratio and oil viscosity) and three results representative of:

1) "volume" aspects under pure rolling conditions with a thick elastohydrodynamic (EHD) oil film.

2) "surface" aspects also under pure rolling conditions but with a thin "incomplete" EHD oil film, i.e. when a high surface roughness to oil film thickness ratio ($\sigma c/ho$) prevails.

3) "surface" aspects with a low slide/roll (0.07) but for otherwise the same conditions as those defined in 1.

They are presented in Table II.

Coating tests

In the same running conditions as before, three types of coated titanium samples were tested against a hard steel roll:

N° 4 T6A4V with plasma Cr_2O_3 coating
5 " " " WC "
6 T6A4V ion beam nitrided by NITRUVID

Test results are presented in Table III.

They show that:

- Chrome oxide coating cracks in pure rolling conditions; probably the coating parameters are not according with the test conditions. Internal stresses have introduced microcracks which extend as soon as high pressures are introduced.
- Samples with WC coating or the nitrided samples withstand the rolling conditions without any degradation.

- When sliding is introduced, seizing that appears with uncoated samples doesn't exist.
- After one million cycles a surface deformation appears with carbide coating.
- Small spalling can be observed on the nitrided surface but without volume degradation.

2.6 - Discussion

These results show that under lubricated conditions the "volume" of uncoated titanium alloy withstands the severe contact conditions imposed.

This remains true for WC coating or after nitriding. Only small losses in fatigue life are introduced with these coatings.

The surfaces are not affected by asperity interactions for the high $\sigma c/ho$ ratio and the high test pressure doesn't introduce any failure in the hard surface layer.

When sliding is imposed on uncoated titanium, seizing appears immediately.

Nitriding the surface in choosen conditions or coating the surface with an adherent hard layer like tungstene carbide, avoids scuffing and seizing and makes possible uses with sliding.

Now these coating parameters have to be improved for each condition to withstand for longer test periods or higher sliding conditions.

3 - TITANIUM ALLOY IN "DRY" FRICTION CONTACTS

The now classical friction log, or 3D plot of friction versus both amplitude and number of cycles, is given in figure 2 for the uncoated titanium alloy tested. The imposed fretting running conditions are marked in the figure.

The log is divided in three parts:

1) surface screens or pollution are eliminated. Adhesion between rubbing surfaces, or first-bodies, is strong and scars are formed in less than 20 cycles.

2) damaged zones strain harden and particles are detached after 20 cycles. Compacted debris form a third-body which is trapped in the contact and often leads to a drop in friction. Debris fragmentation and oxidation occur after 120 or 150 cycles. Total separation is obtained after 800 cycles.

3) three-body contact conditions, characterized by a continuous formation and elimination of debris, are generated. Steady-state conditions prevail. Up to 60 µm thick powder beds are noted after 500 000 cycles (Fig. 3).

These frictions logs are similar to those obtained with other metallic specimens, except for the increase in friction noted at the end of the stroke which can reach 30% of the average stroke value. Such increases, which occur between 100 and 500 cycles, were also observed with aluminium alloys but never with steels. At this time a degradation depth of about 30 µm is observed. This degradation stays constant up to 500.000 strokes.

Titanium alloys are known to have poor rubbing properties. This is a dangerous statement to make, as friction and wear are not intrinsic material properties. Indeed in some instances, debris beds protect the bulk alloy which thus appears to have "good" friction and wear properties, even better than steel. In high frequency fretting test for instance, all steels debris is eliminated from the contact, protection is lost and surfaces are damaged while titanium alloy debris beds are held in place by the rises noted earlier where they can separate and protect the first-bodies.

Figure 3 shows the test results obtained with a nitrided sample tested against an uncoated titanium sample. Friction values are lower, their increasing can be explained by the formation of a protective third body layer. This layer protects titanium against scuffing even if parts of the nitrided layer disappears during tests.

Figure 4 shows results obtained by testing the WC coated samples.

Again here, friction values are low, their decreasing in the first step of running can be explained by surface roughness accommodation.

Surface wear is very small. The contact here exists only between surface roughness peaks; their interaction explain the small rise of friction at the end of the strokes.

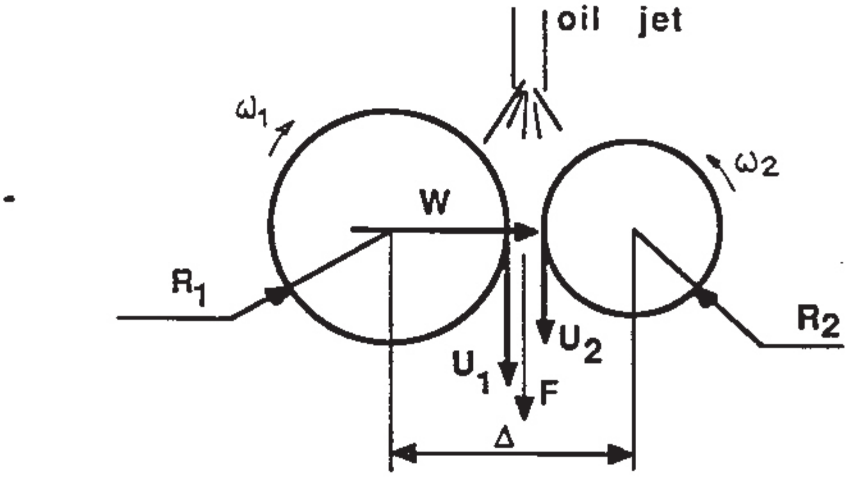
These results show that nitriding or coating titanium with a carbide layer avoid scuffing and give titanium a good wear resistance even at high contact pressures.

4 - CONCLUSIONS

Tribological tests under lubricated hertzian and dry rubbing conditions have been performed on titanium alloys without and with different coatings.

Under lubricated hertzian test conditions, titanium withstands high pressure but sliding induces instantaneous seizing. This scuffing can be retarded to a high number of cycles by protecting the Ti-6Al-4V surface by nitriding or plasma spraying a tungstene carbide coating. Now the choice between these coatings and the optimizing of the deposition parameters: thickness, hardness... have to be done for each specific friction conditions.

PRINCIPLES CHARACTERISTICS OF HIGH PRECISION DISK MACHINE



Center to center distance	Δ (mm)	0 → 100
Disk radius	R_i (mm)	10 → 100
Disk width	(mm)	2 → 15
Rotating speeds	ω_i (rpm)	1500 → 30000
Peripheral speeds	U_i (m/s)	→ 160
Normal load	W (N) /max hertz pressure (GPA)	→ 1500 → 5
Measured friction force	F (N)	3 000
Available power at contact	k (W)	37
Oil jet temperature	T (° C)	→ 200

Any disk material and track roughness

SPECIFIC KINEMATICS CONDITIONS

$U_1 - U_2 / U_1 + U_2$	disk	ω_i (µm)	U_i (m/s)
0	1	8000	15.90
	2	8000	15.91
0.07	1	8570	17.04
	2	7430	14.78

Table 1 - Principles characteristics of high precision disk machine

TEST	CONDITIONS	HERTZ P Gpa	$\frac{U1-U2}{U1+U2}$	EHD film thickness	σ_c	$\frac{\sigma_c}{h_o}$	FAILURE
1	Ti-Ti	1,4	0	1,85	0,5	0,27	None 50 10^6
2	Ti-Ti	1,4	0	0,62	0,5	0,81	"
3	Ti-Ti	0,95	0,07	1,62	0,5	0,31	Immediat seizing

Table 2 - Test results

TEST	CONDITIONS	HERTZ P Gpa	$\frac{U1-U2}{U1+U2}$	EHD film thickness	σ_c	$\frac{\sigma_c}{h_o}$	FAILURE
4	Ti+Cr2O3/ steel	0,95	0	2,58	1,2	0,45	Scuffing at 10^4
5	Ti+WC/steel	0,95	0 0,07	2,58	1,6	0,63	None 50 10^6 deformation at 10^6
6	Ti nitrided/ steel	0,95	0 0,07	2,58	0,77	0,27	None 50 10^6 Small spalling at 5 10^6

Table 3 - Test results

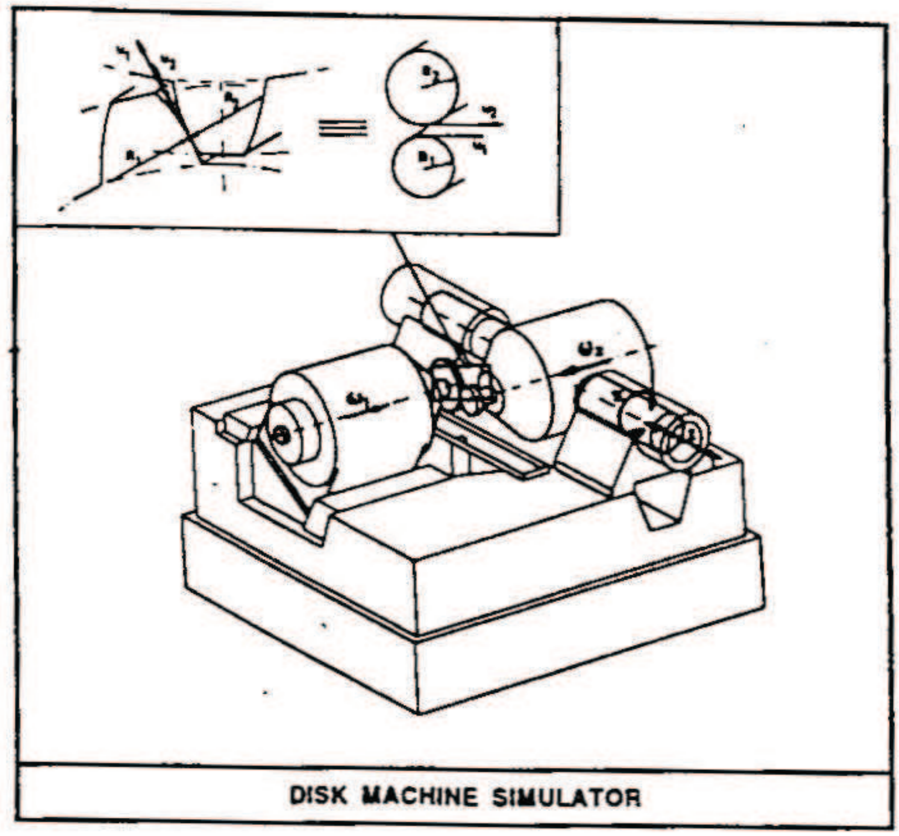


Fig. 1 - Schematic view of disk machine simulator

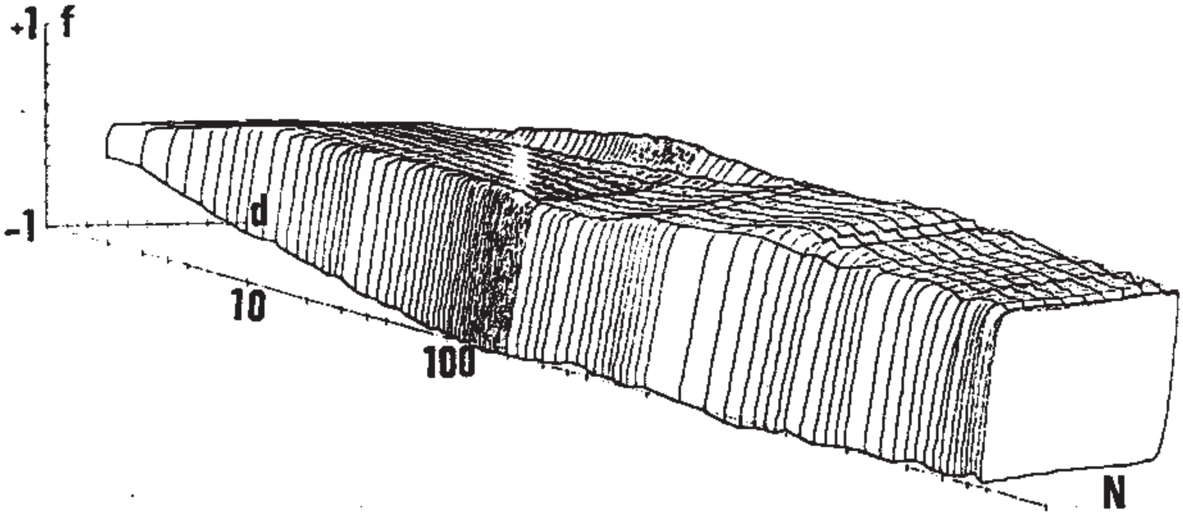


Fig. 2 - Friction log for Ti6Al4V alloy uncoated conditions: load F 500 N, amplitude d ± 50 μm, frequency 1 Hz

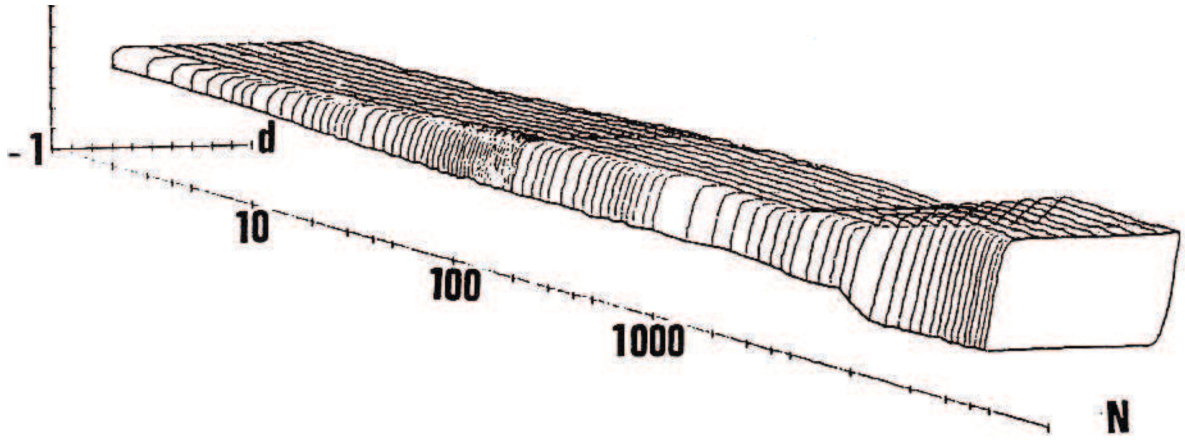


Fig. 3 - Friction log for nitride Ti6Al4V sample

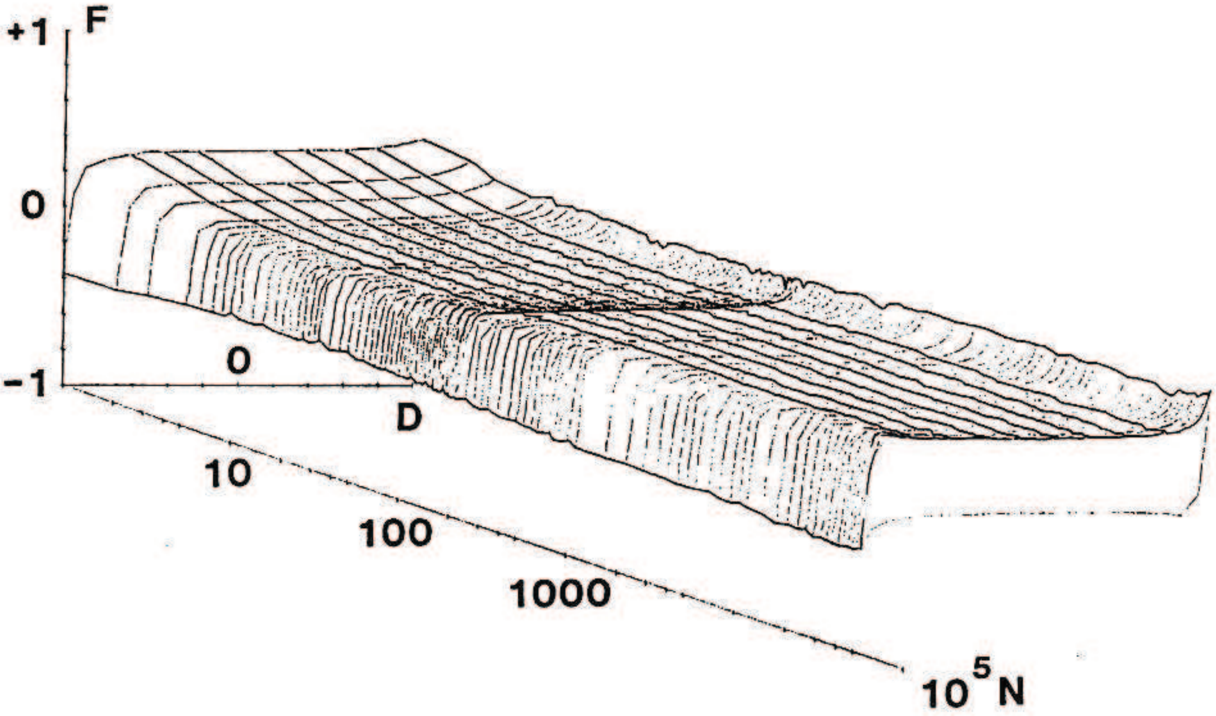


Fig. 4 - Friction log for WC coated Ti6Al4V sample

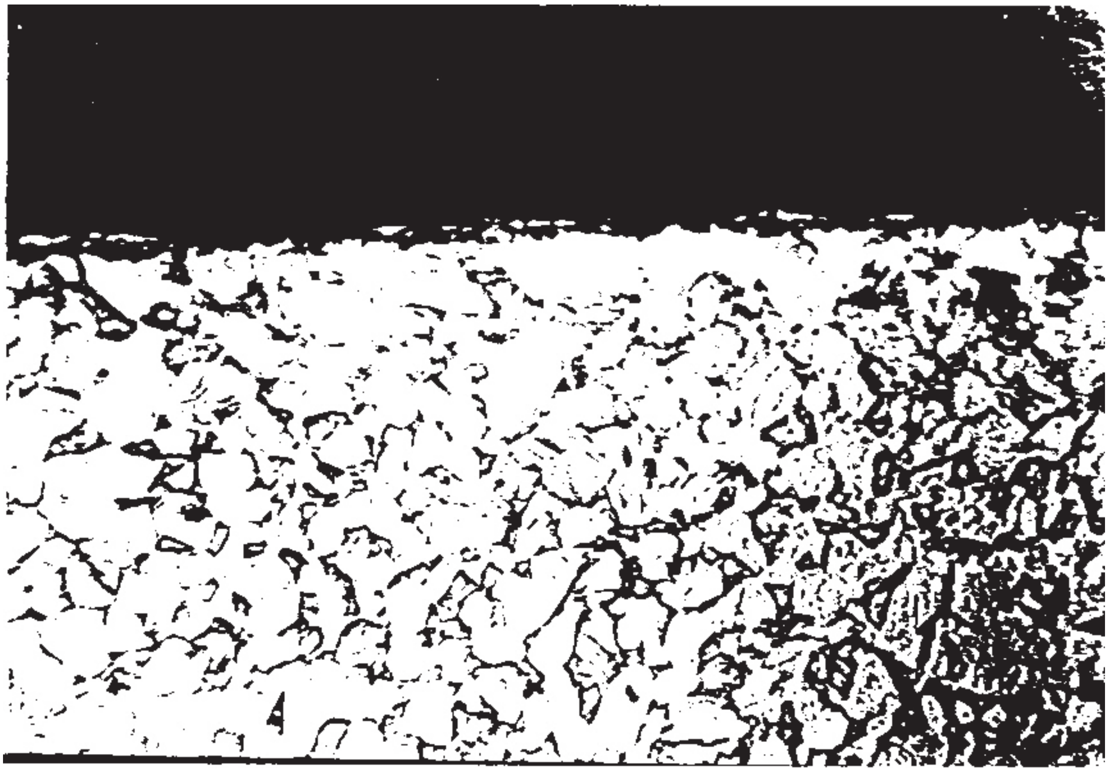


Fig. 5 - Micrographic view of nitride Ti6Al4V tested in friction

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SEGREGATION IN TITANIUM ALLOYS

1 - INTRODUCTION

As in all alloy systems, the mechanical behaviour of titanium alloys is strongly influenced by the way in which the constituent elements segregate on solidification. During the early stages of development in titanium alloys there was a strong tendency to restrict compositions to extremely simple combinations of elements in solid-solution alloys. This trend, coupled with the fact that all titanium alloys initially solidify as single-phase solid-solution β-phase crystals means that segregation problems in titanium alloys are very different from those existing in, say, superalloys or alloy steels. Segregation leading to the precipitation of, for example, congruent melting second phases is essentially absent in this alloy system. On the other hand, segregation cannot easily be dismissed as a problem in titanium alloys because homogenization times and temperatures are excessive. In principle, one might eliminate the segregation of a β-stabilizer in an α/β alloy by long time/high temperature homogenization, but this approach is not feasible on economic grounds. It would require inert atmosphere processing at temperatures approaching 1600°C for many hundreds of hours. We must therefore address the question of reducing ingot

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segregation to an acceptable level by suitably adjusting melting practices.

The concentration gradients represented by segregation are divided by dimension into macrosegregation and microsegregation; the wavelength of the former being ingot radius, that of the latter being the primary dendrite spacing.

2 - MACROSEGREGATION

The constitutional rejection of solute during alloy freezing results in macrosegregation when there is a net bulk displacement between the precipitated solid and remaining liquid, e.g. by fluid flow, or by density separation. The resulting concentration gradients depend on the applicable phase diagram. Although the latter are not available for the complex titanium alloys, we can generalize in some simple cases from the binary diagrams (1) (Fig. 1). Elements which cause a rising liquidus in increasing concentration will segregate negatively (e.g. oxygen) and vice versa (e.g. iron). As a result, the base and edges of a large CP titanium ingot are enriched in oxygen whilst the central core, particularly at the head of the ingot, is enriched in iron.

In what would be normally considered as a remelting process (VAR, ESR, EB etc.), the ingot temperature gradients are sufficiently steep that solidification takes in a columnar dendritic mode, due to a combination of low process temperatures, low melting rates and a predominance of relatively small ingot diameters. The titanium case differs from the above situation (2). The titanium alloys are melted at very high rates (relative to, for example, steels) in order to preserve the surface quality for economic reasons; the consequent process temperatures are high; also the ingot diameter, with few exceptions, are as large as is technically feasible. The result is that the ingot pool is very large and in a typical industrial case only the outer third of the radius solidifies in the columnar dendritic mode. These two features are illustrated in Figures 2 and 3. The central core of the ingot has temperature gradients of less than 18°C/cm which represents the boundary between columnar and equiax solidification for Ti6Al4V under this particular set of flow conditions. The result of this transition is twofold.

First, in the equiax region there exists the possibility of large displacements of solid and liquid by bouyancy forces. Such displacements are responsible for the aluminium variations seen in Ti6Al4V in large ingot sections and are also responsible for the majority of "β-fleck" defects seen in the high-alloy systems. where the β-stabilizing elements segregate positively (e.g. Fe in Ti6Al4V or in Ti-17). The liquidus/solidus gap required to create this situation is not large (Figure 4). In comparison to superalloys, the titanium alloy systems have very small solidification ranges. However, when coupled with the high enthalpy input and low thermal diffusivity of titanium alloys, the result is a ready transition to the equiax mode of solidification.

The second aspect is contained in the flow conditions at the beginning and end of the melting process. The formation of a rapidly-chilled skin of metal at the ingot base (and at the ingot surfaces) takes place in these alloys as a planar solidification front with strong liquid flow over its surface. The solid is therefore in equilibrium with the bulk liquid and we observe a "zone-refining" effect in which the solid is enriched in oxygen, and depleted in alloy elements such as Fe or Cr. As the metal shell thickens the temperature gradients decrease and the planar front degrades to a dendritic one, leading to the familiar columnar dendritic solidification structure, with very little macrosegregation.

At the end of the melting sequence, the liquid metal pool is very large, and as can be seen from Figure 5 the terminating melt-rate sequence is very important in eliminating the resulting shrinkage cavity. During this hot-top process, the temperature gradients are very low and the solidification structure is primarily equiax. The density differences between solid and liquid can lead to a bouyancy-driven macrosegregation although in most titanium alloys this is small.

The solidification of Ti6Al4V, for example produces a primary solid in which the aluminium content is higher than that of the bulk liquid by approximately 0.5 wt%. This segregation is probably not the cause of α-2 defects, but can create problems in precision heat-treatment through its influence on the transus temperature (3) (Figure 6). The segregation caused by the bulk liquid/solid flows in α/β alloys is largely manifest in β-stabilized regions, which although not strongly segregated are sufficiently so to depress the transus below the precise range required for heat treatment. The ranges permitted are small enough that even in Ti6Al4V there can be segregation of iron and copper which is large enough to produce β-fleck. In this alloy also, there is significant dependence of aluminium macrosegregation on melting parameters which has lead to difficulties on occasion in obtaining precise composition control in large diameter ingots.

3 - MICROSEGREGATION

The solidification structure of titanium alloys has not been studied but we may assume that as single-phase solid-solution β-phase precipitates, it will be accompanied by segregation as indicated in the appropriate phase relationships. The dendritic structure is not visible in α or α/β alloys due to the transformation at lower temperature, but the wavelength of segregation within a given primary grain corresponds to that which might result from dendrites with primary spacings of 200-800 µm. The strongly-segregation elements in the interdendritic regions are all β-stabilizers notably Cu, Fe, Ni and Cr. Other β-stabilizers such as Mo do not segregate strongly and do so into the primary solid, not the interdendritic liquid. The normal level of microsegregation has not proved to be a problem in any commercial alloy, but when it is coupled with additional effects it has generated difficulties. The two principal effects are described below.

The high heat input necessitated by the titanium VAR process is concentrated in the region of the active arc. The melting conditions are normally arranged so that this arc is a constricted one, and is quite long (30-40 mm) by the standards of practice in superalloys or steels. The constricted arc is very stable and must be caused to move across the electrode/ingot surfaces by means of an externally-applied magnetic field. The field also causes the liquid metal pool to rotate. Both of these effects are used to re-distribute the incoming heat flows to the pool so that the ingot axial surface temperature is maximized and the surface quality maintained. The thermal disturbances which accompany the above effects, however, also cause irregular growth of the solidification front, with accompanying variations in the local microsegregation. The result is a pattern of concentric paraboloids of segregation changes which when intersected by a radial cut appear as "tree rings" on the radial surface (Figure 7). The etching effect is highly visible, but as yet it has not been established that the segregation is sufficient to cause any mechanical property changes. Similar effects in steels have been shown to cause a decrease in LCF life of approximately 10%, but at much higher relative strength levels than are used in titanium alloys.

The second major effect is that of "freckles" (3). The bulk liquid pool movement interacts with interdendritic liquid to form channels in the dendrite network. This defect is well-known in other, lower melting-point systems and represents a very serious mechanical property problem in the product. The channel flow is density-driven and since it requires relatively large changes in density as the interdendritic liquid is formed, the mechanism is very seldom found in the present range of commercial alloys. However, it can, and does, exist in these materials (Figure 8).

4 - DISCUSSION

The specific kinds of segregation found in titanium alloys must be eliminated by suitable changes in the melting practice and cannot be rectified by homogenization and /or mechanical working. Since the VAR process requires a high heat input to maintain surface quality, it is also clear that the options for solidification control are severely limited. Indeed, it is already probable that the practical limits have been reached in respect of melting rates and ingot diameter for the present range of commercial alloys.

The limiting feature of VAR is the direct linkage between melting rate and power input. For solidification control we must un-link these two parameters, as is achieved in either EB or plasma melting. Once this aim has been satisfied, we can increase the ingot temperature gradients to the point at which the condition of 100% columnar-dendritic structure is obtained and macro-segregation is absent. At the same time, by removing the need for strong external electromagnetic stirring, the fundamental cause of the microsegregation defects will have also been removed. The result will be a more uniform ingot composition and also the possibility of making the segregation-sensitive grades in larger ingot diameter should this prove necessary in the future.

5 - REFERENCES

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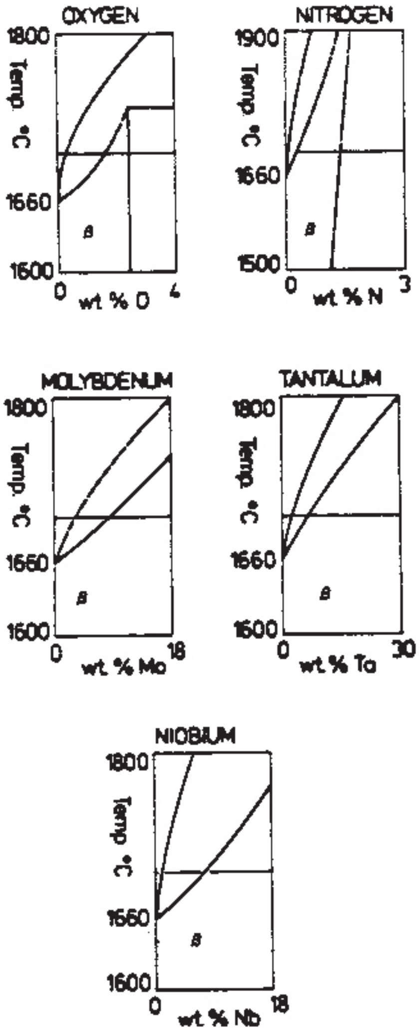


Fig. 1A - Phase diagrams for solid stabilizing elements in titanium in the titanium rich region.

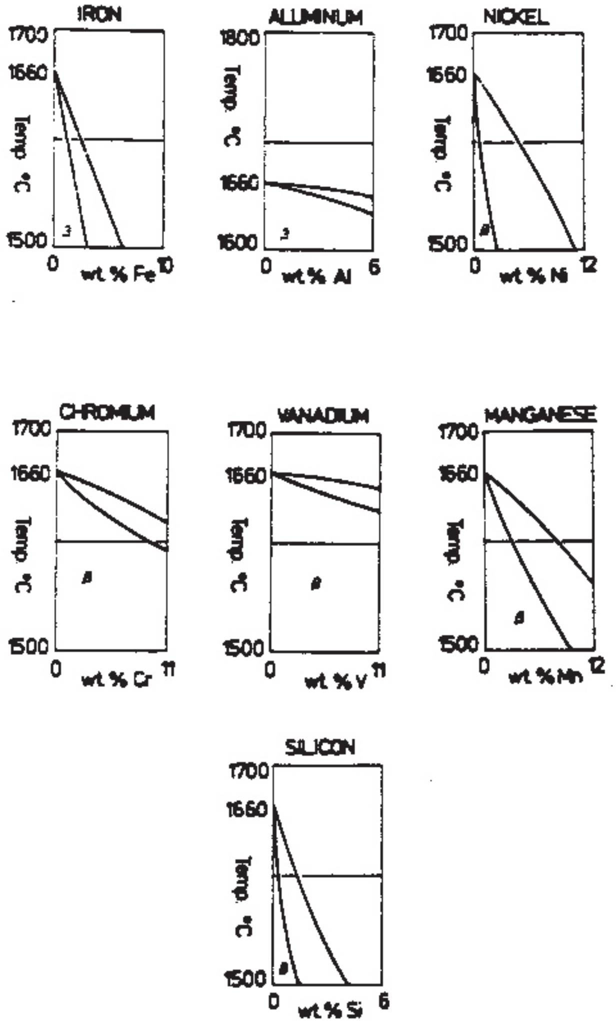


Fig. 1B - Phase diagrams for solid stabilizing elements in titanium in the titanium rich region.

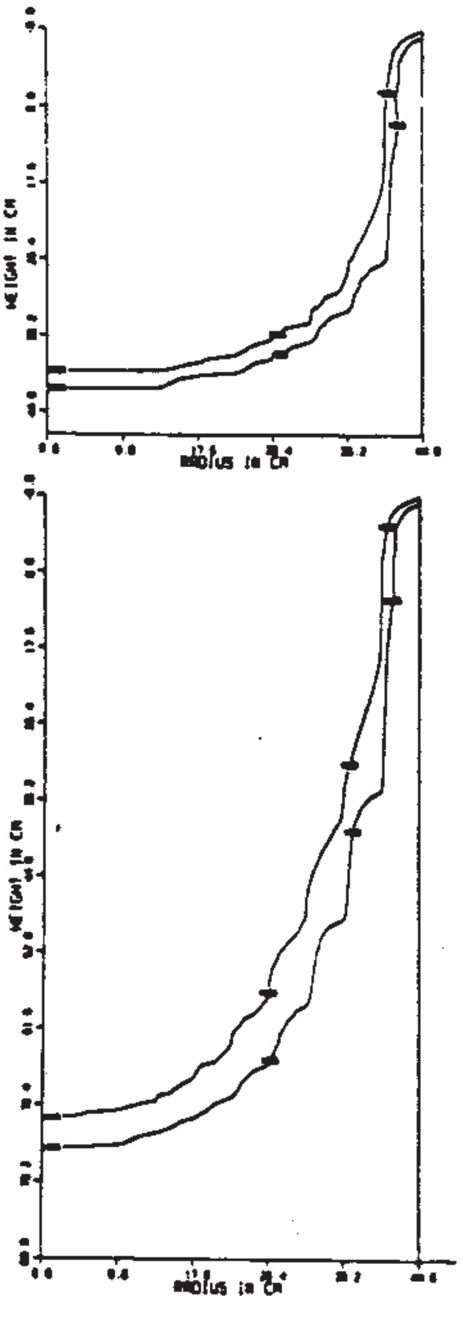


Fig. 2A - Liquidus-solidus profiles in an ingot of Ti6Al4V (VAR) at a melting rate of 700 kg/hr during the initialstages of melting.

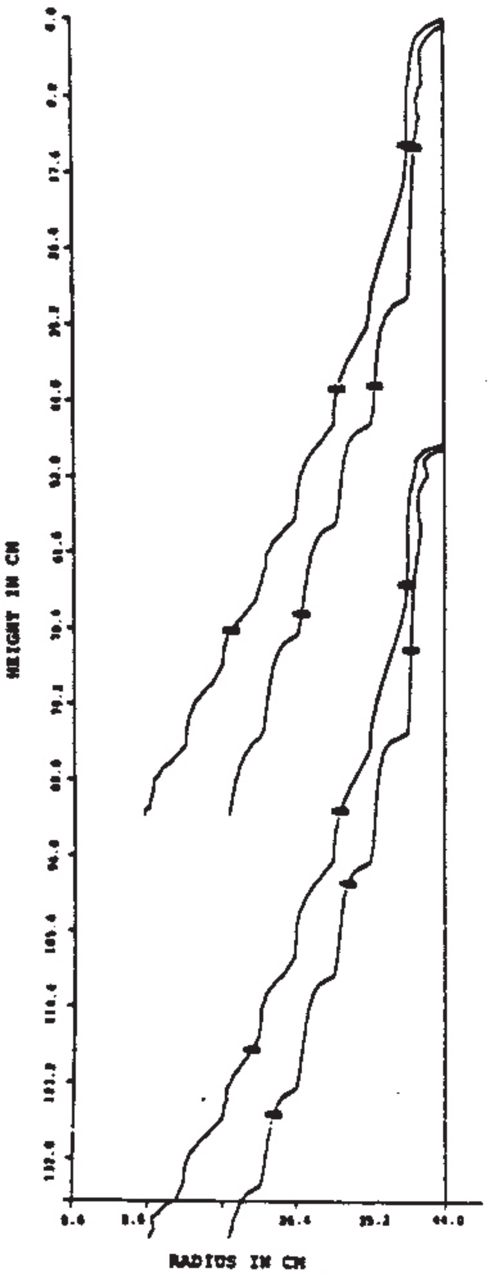


Fig. 2B - Liquidus-solidus profiles in an ingot of Ti6Al4V (VAR) at a melting rate of 700 kg/hr during the final stages of steady state melting.

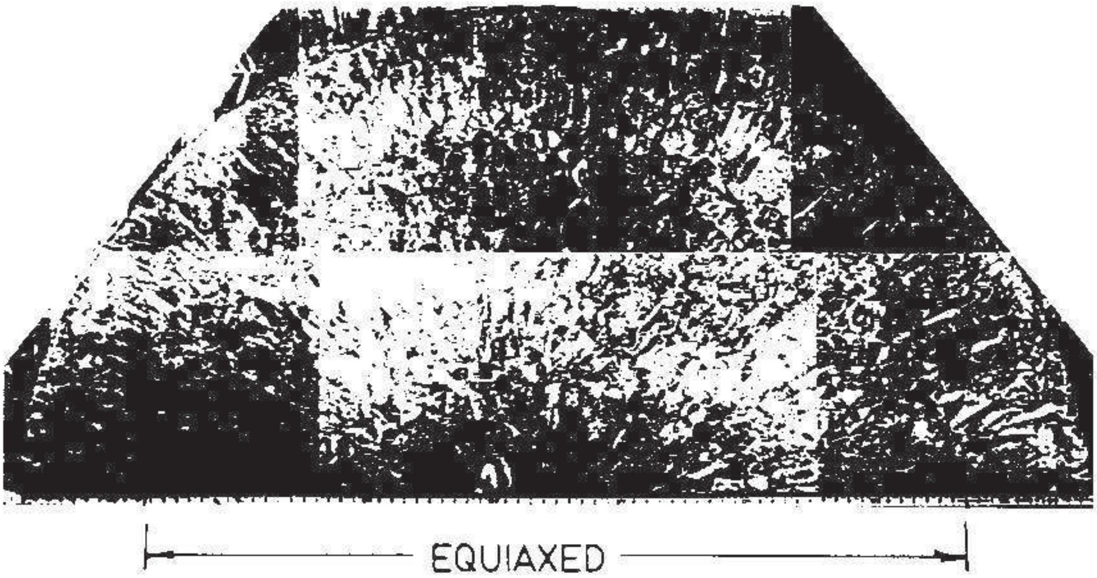
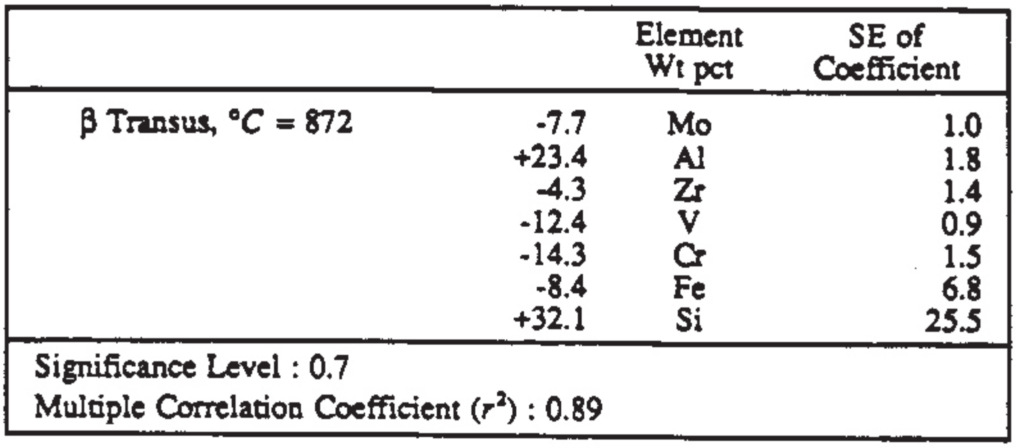


Fig. 3 - Ingot structure in a VAR ingot of Ti6Al4V showing the transition from columnar dendritic to equiaxial grain growth at the mid section of the ingot shown in fig. 2



		Element Wt pct	SE of Coefficient
β Transus, °C = 872	-7.7	Mo	1.0
	+23.4	Al	1.8
	-4.3	Zr	1.4
	-12.4	V	0.9
	-14.3	Cr	1.5
	-8.4	Fe	6.8
	+32.1	Si	25.5

Significance Level : 0.7

Multiple Correlation Coefficient (r^2) : 0.89

Fig. 4 - Liquidus and solidus temperatures for various commercial titanium alloys.

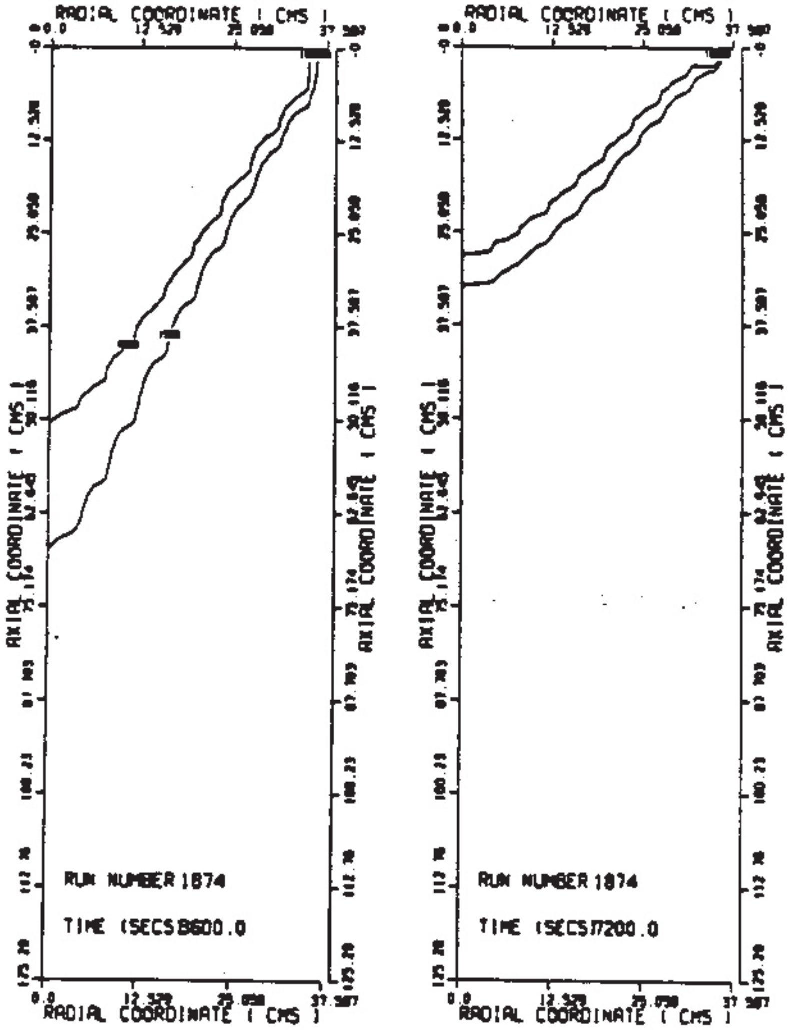


Fig. 5A - Liquidus-solidus profiles in an ingot of Ti6Al4V (VAR) during the hottop sequence.

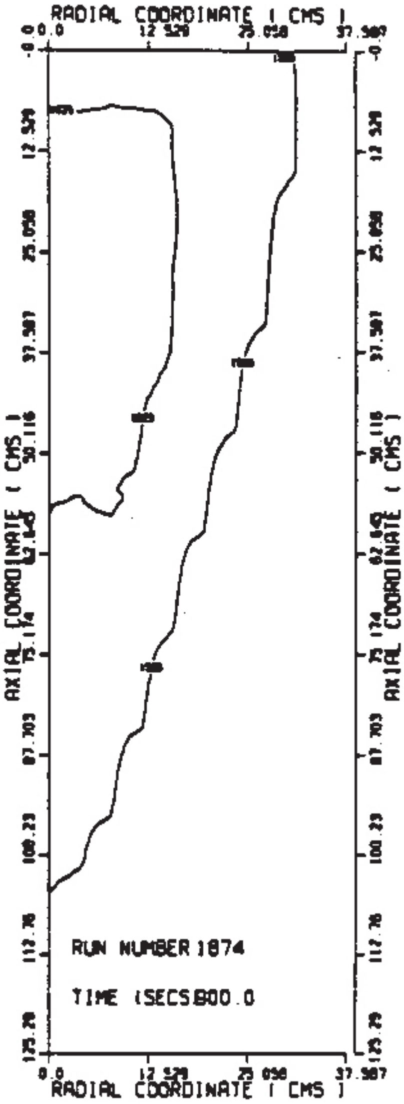
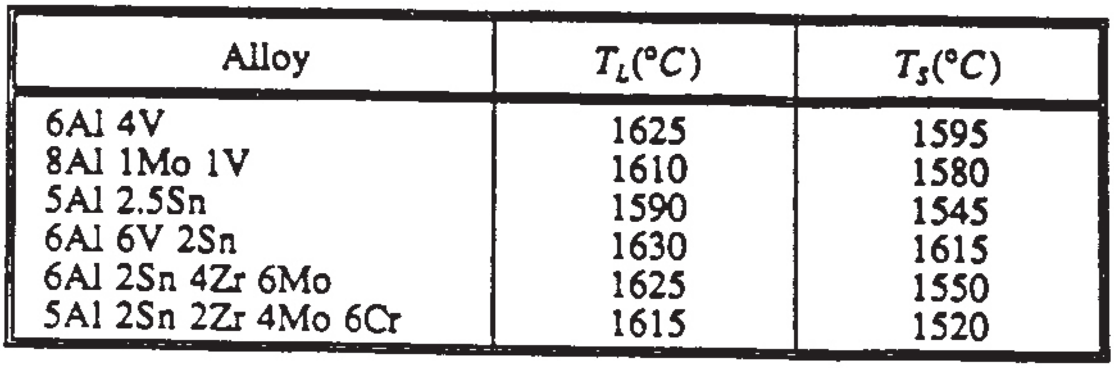


Fig. 5B - Liquidus-solidus profiles in an ingot of Ti6Al4V (VAR) after steady-state melting using no hottop sequence.



Alloy	T_L(°C)	T_S(°C)
6Al 4V	1625	1595
8Al 1Mo 1V	1610	1580
5Al 2.5Sn	1590	1545
6Al 6V 2Sn	1630	1615
6Al 2Sn 4Zr 6Mo	1625	1550
5Al 2Sn 2Zr 4Mo 6Cr	1615	1520

Fig. 6 - The variation of Beta transus temperature with composition for various alloying elements in titanium.

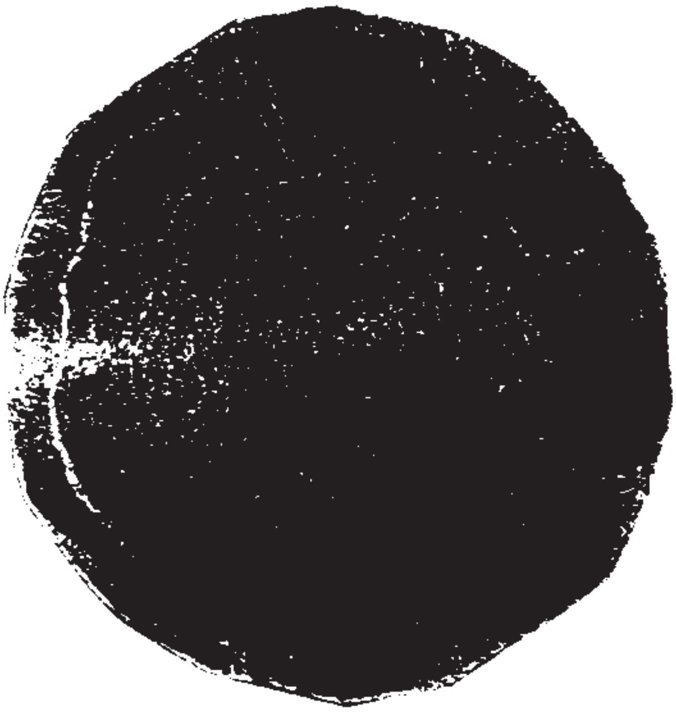


Fig. 7A - Tree-rings in Ti-17 alloy

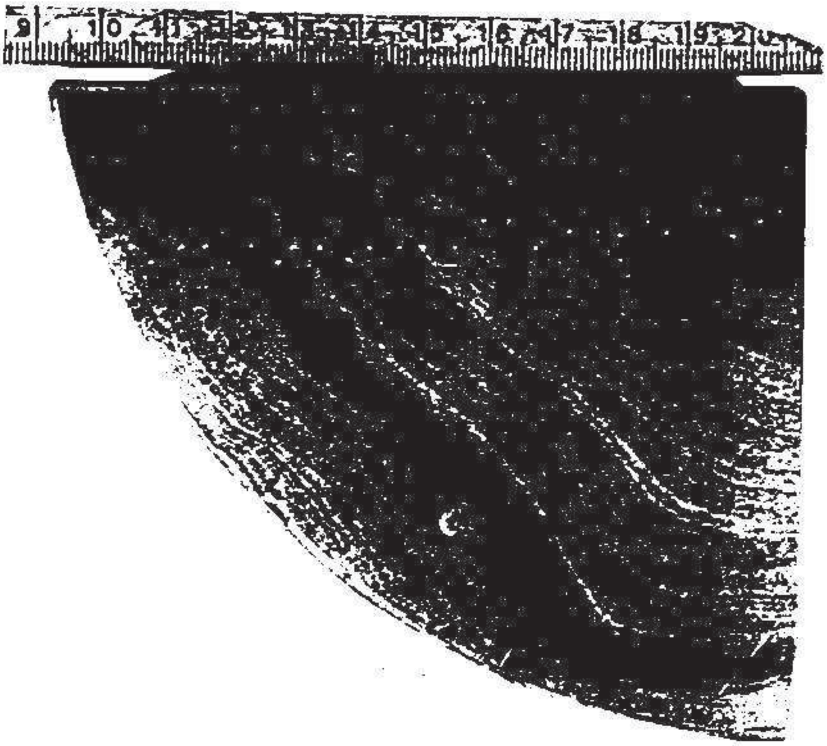


Fig. 7 - Tree-rings in Ti6Al2Sn4Zr6Mo alloy

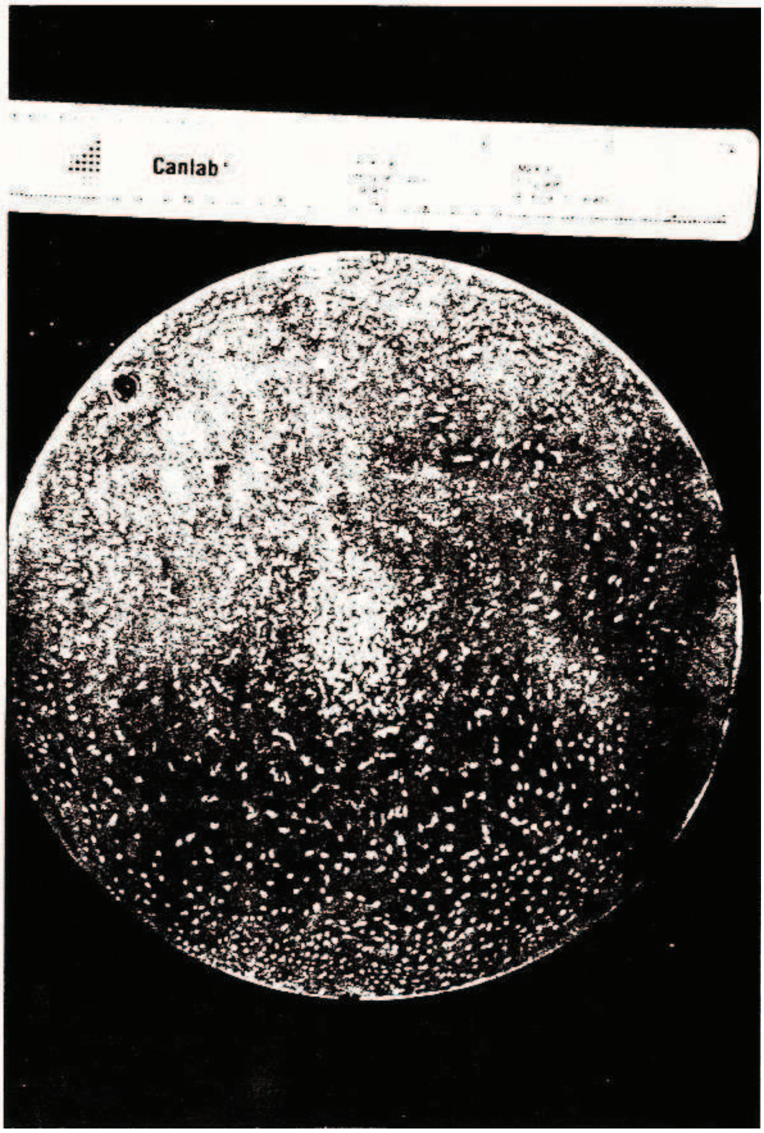


Fig. 8 - Freckles in a near-beta alloy

Carlos Aguirre
Axel Johnson Metals, U.S.A.

CASTING TITANIUM SLABS IN AN ELECTRON BEAM FURNACE

Good afternoon. There is a coauthor of this paper, Charles Entrekin, who couldn't come with me and he told me he will answer any questions by mail. Five years ago we presented a paper at the "Vacuum Metallurgical Conference" at Pittsburgh to describe direct casting of titanium slabs that we pioneered in the early 80's.

Today, more than 3,000 metric tons of titanium slabs have been cast and made into milled products and the objective of this presentation is to give an update on the status of titanium cast slabs, to make a comparison between the cast slabs and the conventionally made slabs, either by rolling or by forging and then to provide some guidelines for product optimization.

Axel Johnson (Fig. 1) started a scrap process for titanium in the early 70's and in 1983 we decided to expand our operation into an electron beam furnace and this technology was a logical extension for us because really the electron beam was a very efficient way to recycle titanium scrap. In only one melting step titanium scrap is transformed into semi-finished form and in that way we maximise the added value.

Our electron beam operation is located in Morgantown. It has a 2 MW cold hearth EB furnace so we got 4 EB guns of 600 kW each. Melting rates range between 0.5 and 1.5 metric tons per hour depending on the product requirements. The process has shown significant versatility in raw material feedstock. The furnace can be fed with various types of particulate scrap blends including turning solids and titanium sponge as well as large bars or electrodes for remelting. Initially we produced small slabs of 2 metric tons but the yields and the productivity were not optimum. So in 1985 we developed a larger 5 metric ton slab that has been very, very successful. At the present time we are developing a capability for producing up to 15 metric ton slabs.

This is a schematic view of our furnace (Fig. 2). We have a melting chamber, the electron beam guns are at the top of the furnace. On the right we have the feeding chamber where particulate scrap is fed into the hearth and then we have an ingot chamber that can be removed so that we can pick up an ingot. All this is done under high vacuum.

Here we can see a remelting or casting of a slab and to us this is one of the great things of this process, the casting flexibility, we can really cast any cross-section, any geometrical shape. This is possible because we can position the energy in discrete amounts in any place of the mould and that allows us very good control on the solidification conditions.

In Fig. 3 there is a view of a 2 metric ton slab. The dimension are 6" in thickness by 28" in width and 130" long. The largest slab is 12" thick and 44" wide and about 4.5 meters long.

In Fig. 4 we see 2 slabs that have been conditioned, machined on the surface.

In Fig. 5 we are trying to make a comparison between the normal conventional processing of a slab and an electron beam slab, the cast slab. This is similar, like in steel where you have the old way to make a slab and then you have continuous casting. In the conventional case we can use scrap or sponge, then we have to recompact it, an electrode has to be assembled, then there are two VAR steps and then we have a chamber step with an overall yield, metallic yield of about 96%. In an electron beam we can just blend scrap and sponge and we make it in one melting step, we end up with the slab. We condition and the yield at that point is about the same. But in the first case we have a round ingot, in the second case we have a slab already.

Continuing the processing, the ingot has to be forged or rolled into a slab and then conditioned and all the way to flat rolled product, with an overall yield of about 65%. lf we do it with a slab from an EB, we get about 70% overall yield and that's about 8% better than the conventional forming.

The grain structure of the EB slabs shows a typical solidification structure. It's coarser than a forged or rolled slab. Conventional slabs have recrystallized grain, resulting from the mechanical work associated with the transformation from a round ingot into a slab form.

In the EB process, the slab are hot-topped to minimize the shrink or cavity, but on occasion some porosity is present. This characteristic does not yield harmful results because the total defects are healed during the further rolling or processing. Detecting small pipe porosity in a cast slab by ultrasonic testing is difficult because the core solidification structure interferes with the V.T. response. Only large pipe defects can be detected. We feel that this is adequate because the small porosity defects are harmless and do not affect the product yield and disappear upon further processing. Really, these small porosities are inside defects, there is no connection to the atmosphere, to the air and so when you roll they heal.

As is the case with most cast products, the cast surfaces of the slab are not adequate for rolling, so we have to condition the slabs. Machining, we have found, produces better results than grinding.

Typical chemical composition of slabs: the normal grades 1, 2, 3, 4, 7 and 12 of CP and also in Fig. 6 we have put some typical Japanese grade 1 slabs and some Soviet slabs. And if you compare those with the grade 1 that we make, the first one in that list, you will see that there is some higher residual elements, higher carbon, higher oxygen, higher iron and then aluminum and a little bit of nickel, molybdenum and vanadium. This is because we work with blends of scrap and there is always some residual elements in scrap as compared with the other two cases where people used pure sponge. The one thing that we have is lower nitrogen and hydrogen content. Hydrogen is normally below 10 ppm and nitrogens are less than 100 ppm.
These types of residual elements have not shown harmful effects from the view point of corrosion properties, however they do affect the yield strength of the material. On the other hand the elongation and ductility of the product coming from EB slabs are enhanced and we think this is because of the lower hydrogen and nitrogen content.

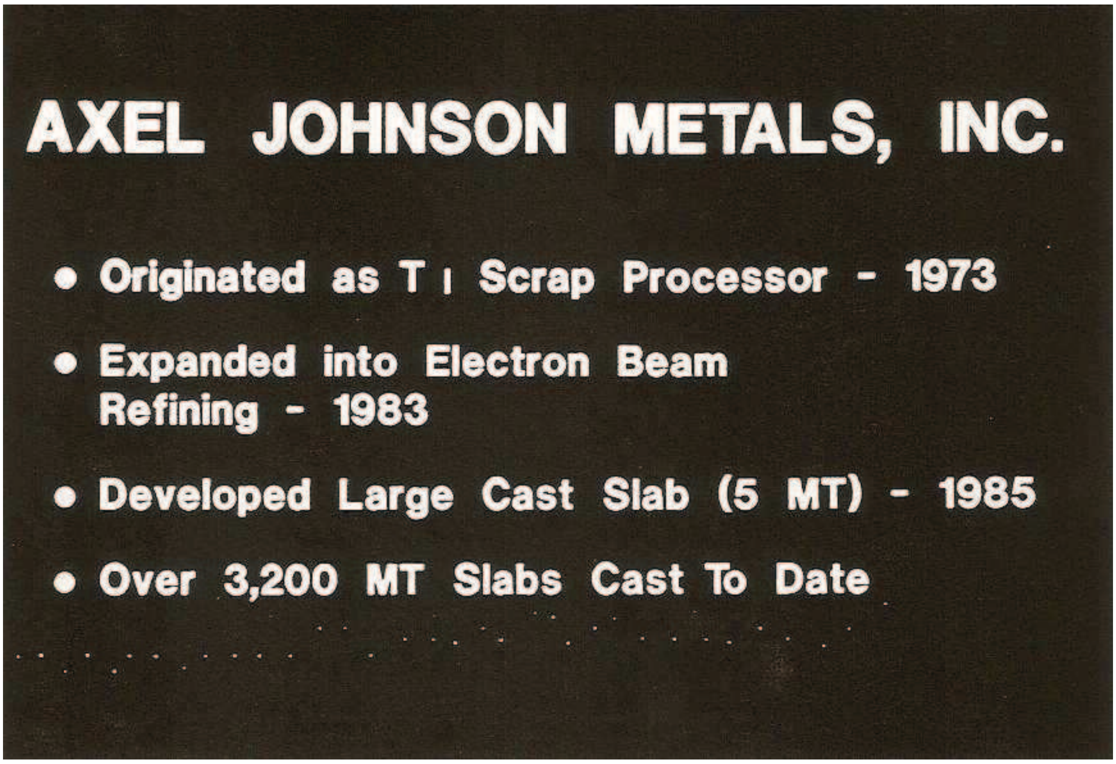
To relate the mechanical properties of commercially pure titanium, an oxygen equivalent formula is used. These formulas are empirical in nature and relate the effects of various elements to the strengthening effects of oxygen. There are several versions, the first one is attributed to Timet where they show that nitrogen has 2.5 times the effect of strengthening than oxygen and iron about half. Then there was another formula we call the Timet modified that added also the effect of carbon. On the other hand, RMI has also a formula that doesn't show the effect of iron but just considers carbon and nitrogen and that's because they work with very low iron contents. In order to understand the mechanical properties of products produced from our slabs, we had also to include another element and that is aluminum, and we call that the A. Johnson oxygen equivalent. Normally this equivalent oxygen is one or two points higher than the one predicted by the Timet or the RMI formulas. We have tried to relate the oxygen equivalent to the mechanical properties and in table 8 we show levels of oxygen equivalent we need to develop the mechanical properties for the different grades.

If products made from our slabs are heat treated the same way as conventional products, we end up with yield strengths that are the higher side of the range. If we look at the microstructure we find that the grain size of the product from our slab is about 0.5 of the size of the conventional product.
We believe that the residual elements slow down the grain growth and what we are suggesting is that higher annealing temperatures are necessary to get the yield strength a little bit on the lower side. So we recommend a rolling temperature 900-980°C, an annealing temperature around 850°C: that's about 50° higher than the conventional temperature for strip. Then, for plate we need lower temperatures: about 780°C (Fig. 9).

So, to finalize this presentation, these titanium slabs have been a great technical and commercial success over the last 5 years and they are regarded, in some cases, as the standard product for most applications. They have proved to be extremely convenient and an economic method to recycle very large proportions of titanium scrap. Their uniform rectangular shape and internal soundness have provided the users with up to 8% higher yields. The mechanical properties of these milled products are equivalent to those of conventional products and it can be tailored to most applications if the proper heat treatment is used. Many slabs are now produced in electron beam furnaces from standard raw material charge consisting of 15-25% sponge, and sponge is a problem in our furnace if the chloride content is high. At the present time we are really watching the development of the electrolytic sponge technology because we think it can be very compatible with our furnace.

Finally I want to add an announcement that the Axel Johnson method has received recently approval to proceed with the design and construction of a second EB furnace in Morgantown, Pennsylvania. This furnace will be a next generation furnace, featuring at least 3 MW in power, maybe 4, and it will have two melting chambers. This unique furnace design, we call it maximelt, because we are trying to maximize productivity, is a result of our experience with the first furnace and we are really looking forward to starting production in the first quarter of 1990.

Thank you!



AXEL JOHNSON METALS, INC.

- Originated as Ti Scrap Processor - 1973
- Expanded into Electron Beam Refining - 1983
- Developed Large Cast Slab (5 MT) - 1985
- Over 3,200 MT Slabs Cast To Date

Fig. 1 - Axel Johnson development

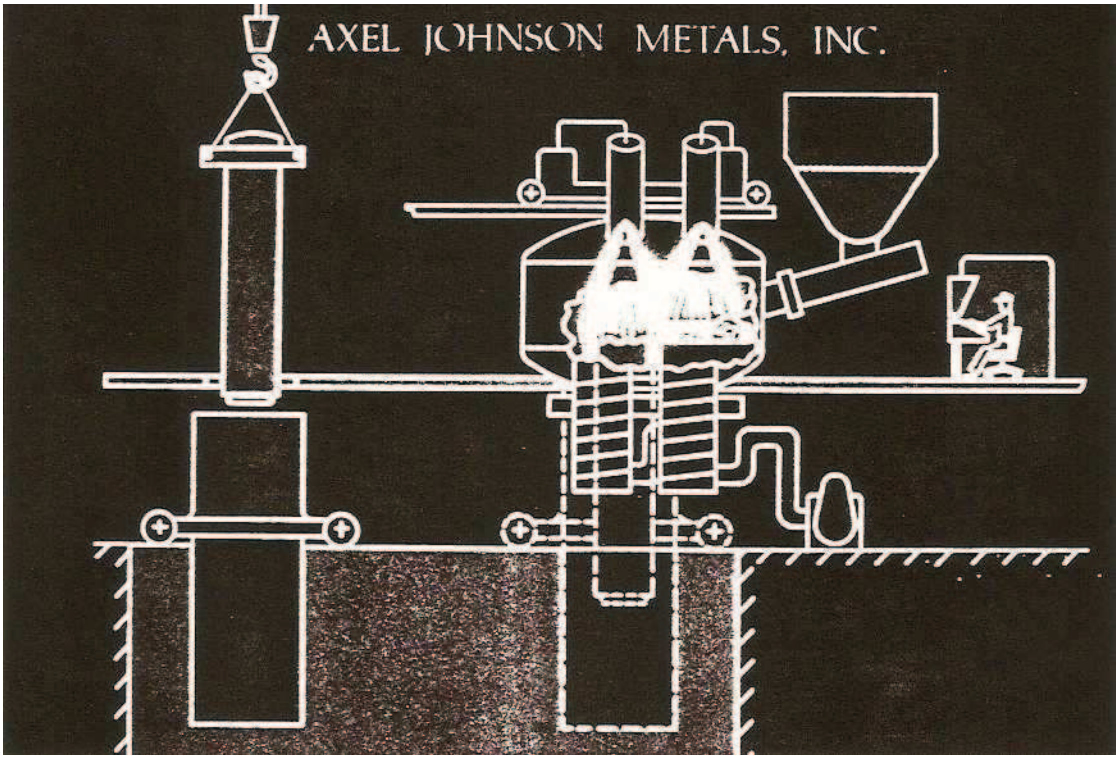
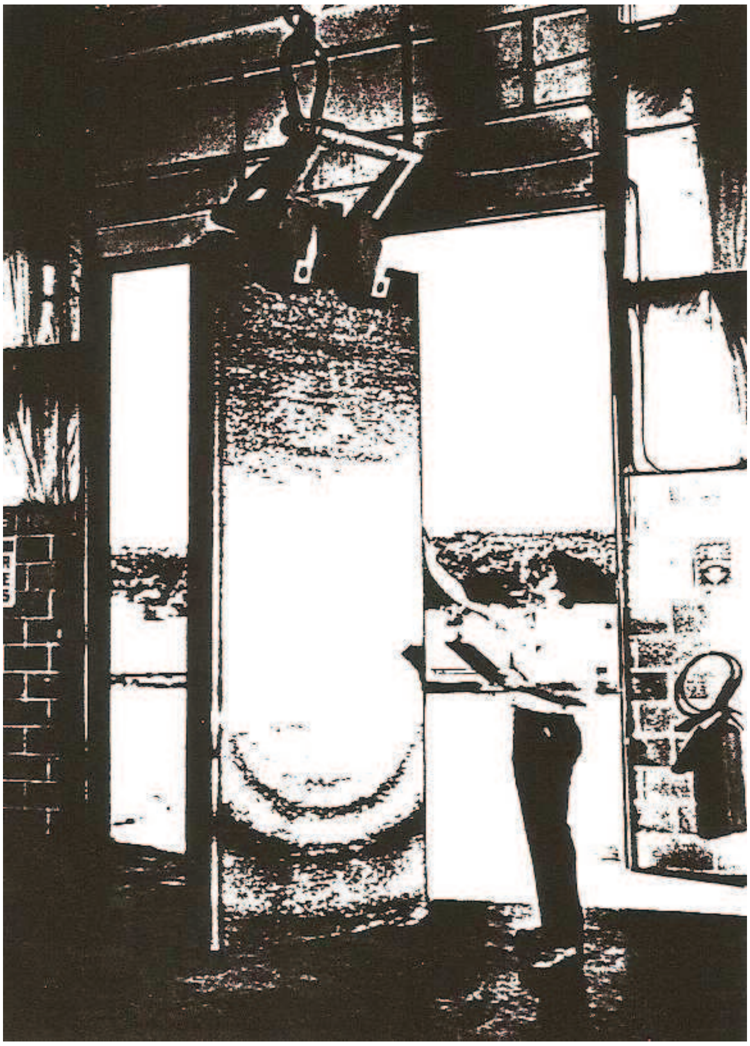


Fig. 2 - Schematic view of Axel Johnson Electron Beam Furnace

Fig. 3 -
2 metric ton slab



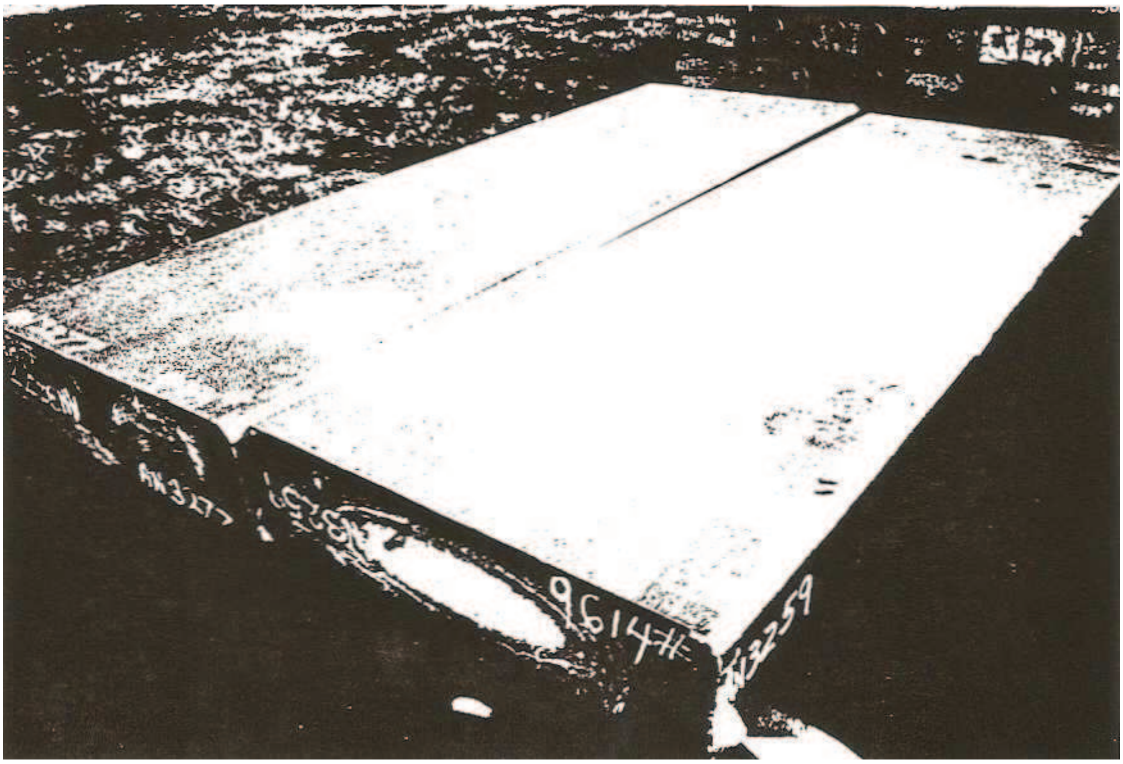
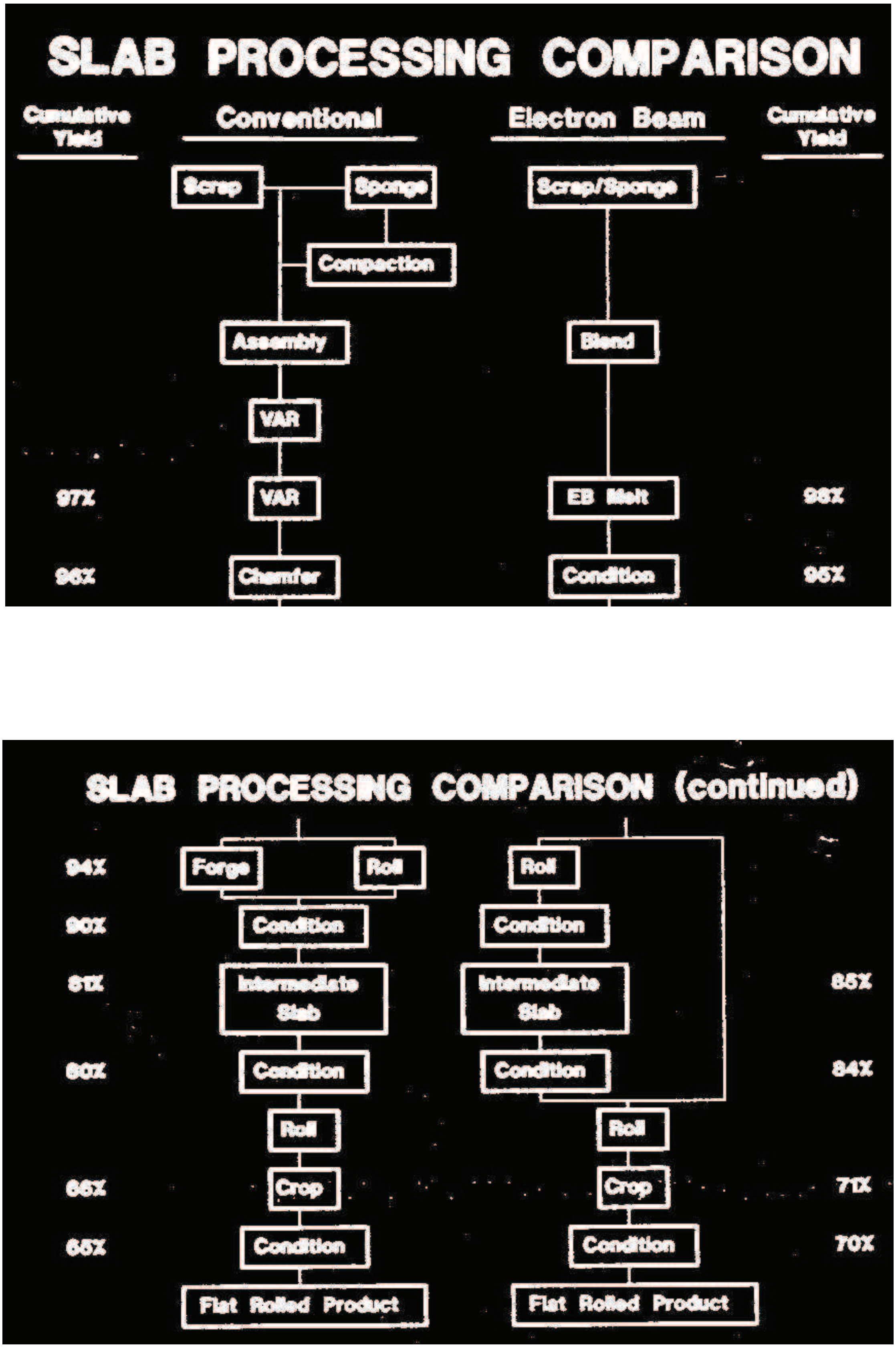


Fig. 4 - Electron Beam melted slab, machined surface



SLAB PROCESSING COMPARISON

Cumulative Yield

Conventional

Scrap

Sponge

Compaction

Assembly

VAR

97% VAR

96% Chamfer

Electron Beam

Cumulative Yield

Scrap/Sponge

Blend

EB Melt 98%

Condition 95%

SLAB PROCESSING COMPARISON (continued)

94% Forge Roll

90% Condition

81% Intermediate Slab

80% Condition

Roll

66% Crop

65% Condition

Flat Rolled Product

Roll

Condition

Intermediate Slab 85%

Condition 84%

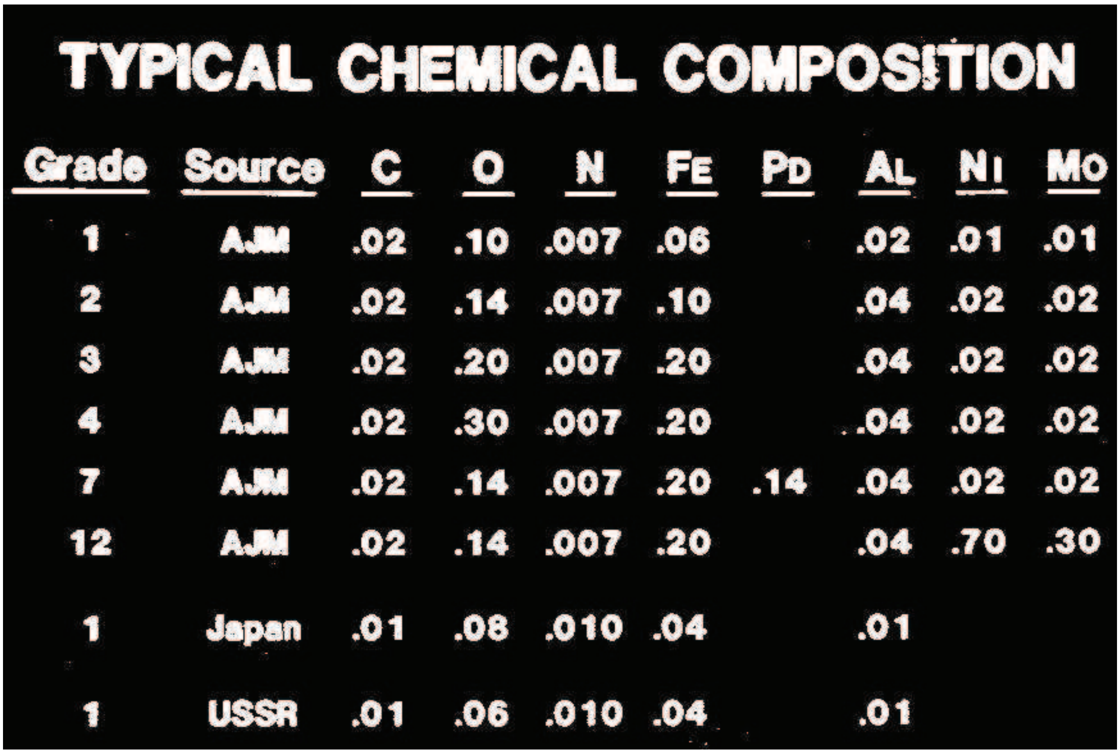
Roll

Crop 71%

Condition 70%

Flat Rolled Product

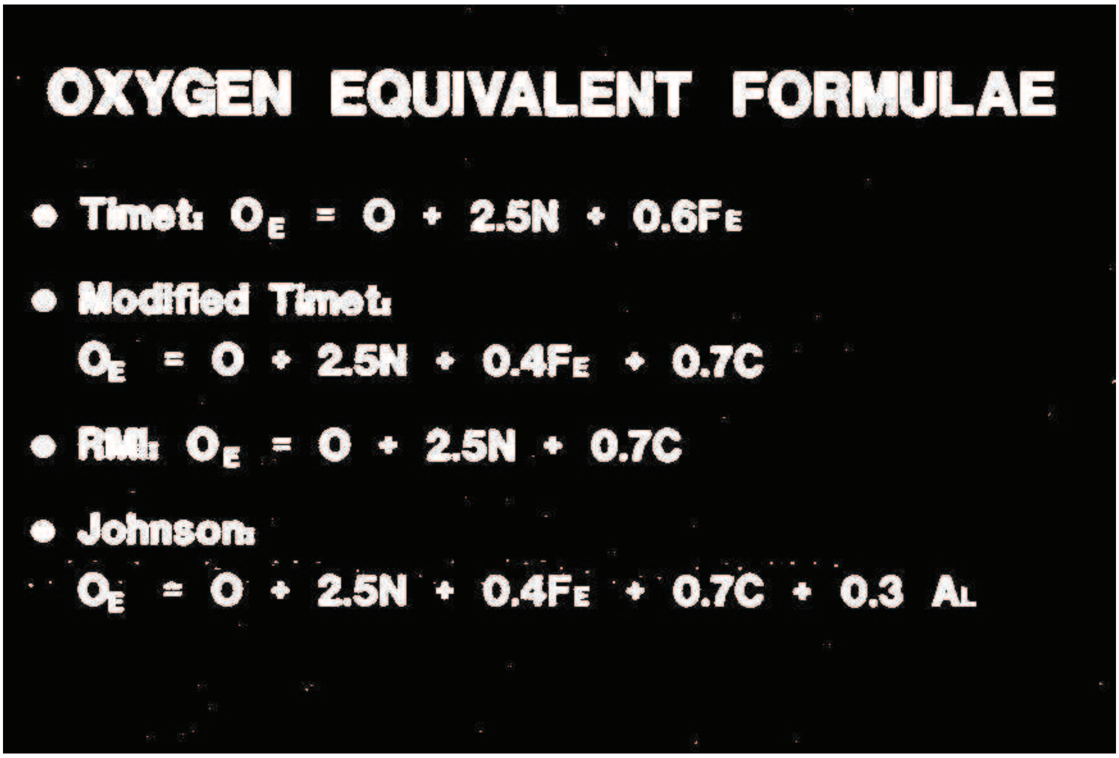
Fig. 5



TYPICAL CHEMICAL COMPOSITION

Grade	Source	C	O	N	FE	PD	AL	NI	MO
1	AJM	.02	.10	.007	.06		.02	.01	.01
2	AJM	.02	.14	.007	.10		.04	.02	.02
3	AJM	.02	.20	.007	.20		.04	.02	.02
4	AJM	.02	.30	.007	.20		.04	.02	.02
7	AJM	.02	.14	.007	.20	.14	.04	.02	.02
12	AJM	.02	.14	.007	.20		.04	.70	.30
1	Japan	.01	.08	.010	.04		.01		
1	USSR	.01	.06	.010	.04		.01		

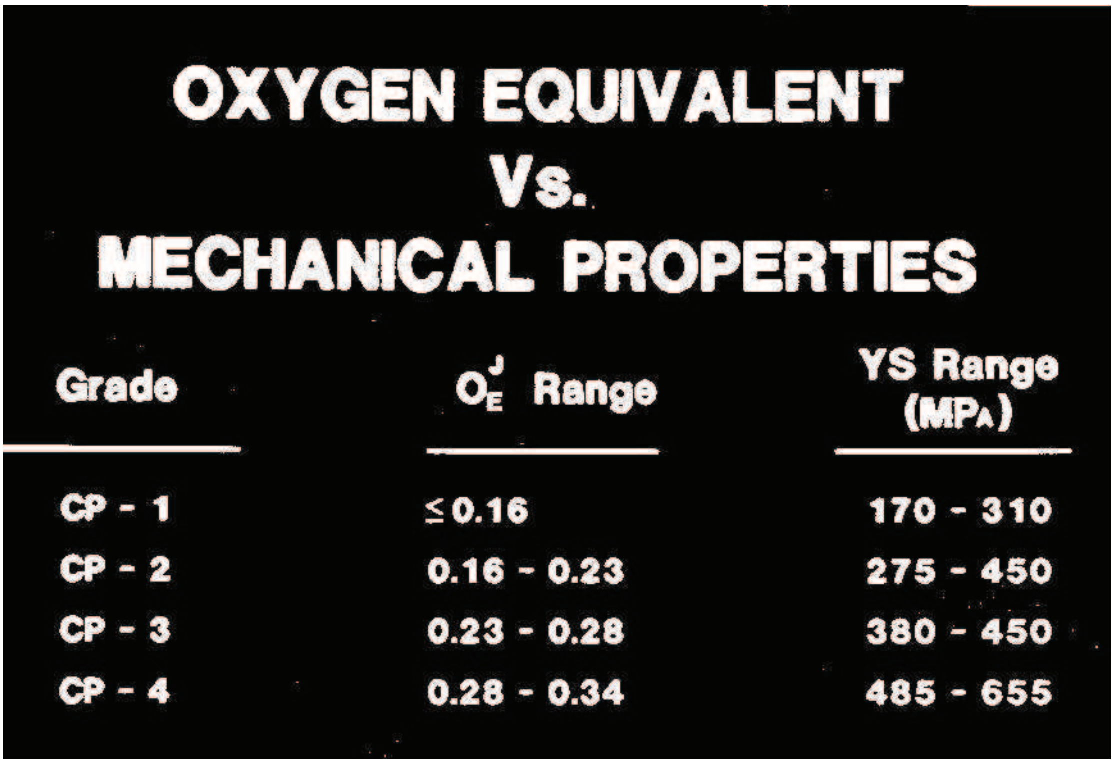
Fig. 6



OXYGEN EQUIVALENT FORMULAE

- Timet: $O_E = O + 2.5N + 0.6Fe$
- Modified Timet:
  $O_E = O + 2.5N + 0.4Fe + 0.7C$
- RMI: $O_E = O + 2.5N + 0.7C$
- Johnson:
  $O_E = O + 2.5N + 0.4Fe + 0.7C + 0.3\,Al$

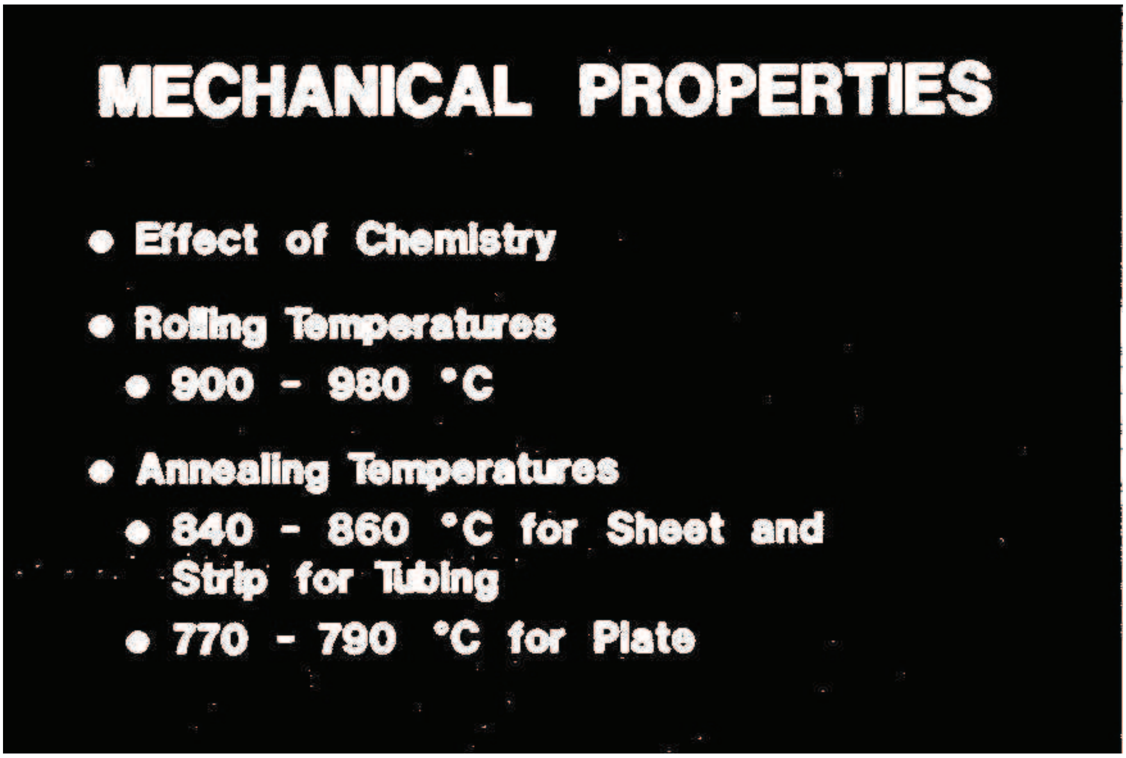
Fig. 7



OXYGEN EQUIVALENT
Vs.
MECHANICAL PROPERTIES

Grade	O_E^J Range	YS Range (MPA)
CP - 1	≤ 0.16	170 - 310
CP - 2	0.16 - 0.23	275 - 450
CP - 3	0.23 - 0.28	380 - 450
CP - 4	0.28 - 0.34	485 - 655

Fig. 8



MECHANICAL PROPERTIES

- Effect of Chemistry
- Rolling Temperatures
  - 900 - 980 °C
- Annealing Temperatures
  - 840 - 860 °C for Sheet and Strip for Tubing
  - 770 - 790 °C for Plate

Fig.9 - Modified heat treatment for Electron Beam melted slabs

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APPLICAZIONE DEL TITANIO NEL RESTAURO STATICO DELLA COLONNA ANTONINA IN ROMA

Nel corso dei lavori di restauro delle superfici lapidee delle Colonne Coclidi in Roma, la visione ravvicinata dei rocchi dal ponteggio e il loro quadro d'insieme fornito dall'attuale rilievo hanno messo in luce una complessità di progetto e alcune problematiche strutturali poco approfondite dagli studi fino ad oggi intrapresi. Tale trascuratezza è forse da imputare nell'interesse che sempre esercita sull'osservatore il nastro figurato spiraliforme scolpito sul fusto dei due monumenti. Alla luce delle nuove osservazioni la Soprintendenza Archeologica di Roma ha affidato, nel maggio 1986, a tecnici del Dipartimento di Ingegneria Strutturale e Geotecnica dell' Università "La Sapienza" (1), la valutazione della sicurezza sismica della Colonna Traiana e della Colonna Antonina e lo studio degli interventi di restauro statico resi necessari dallo stato di degrado di alcune delle strutture lapidee.

Le due colonne, la prima presso Piazza Venezia e la seconda in Piazza Colonna, si presentavano con problemi analoghi ma con quadri fessurativi sostanzialmente diversi: i terremoti passati, in special modo quello del 1349, lasciarono evidenti segni nella Colonna Antonina: i pesanti rocchi, svuotati

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Coautore:
Fabio Ortolani, Università "La Sapienza"

all'interno per la presenza della scala a chiocciola, appaiono ruotati e traslati. Danni della stessa natura sono presenti, ma in modo meno evidente, nella Colonna Traiana. L'esame dei quadri fessurativi ha evidenziato che gli spostamenti interessarono principalmente i rocchi che avevano già perso l'originale monoliticità a causa di fattori legati sia alla struttura intrinseca della pietra sia a cause accidentali esterne come, ad esempio, i fulmini (2).

La Colonna Antonina si presentava a metà del sec. XVI in condizioni che facevano temere per la sua stessa stabilità tanto da far dichiarare a Domenico Fontana, incaricato dal Papa Sisto V di restaurare le colonne, che essa " ... stava per ruinare ... ". Nei disegni eseguiti nella prima metà del '500 è ritratto l'ampio squarcio a 3/4 del fusto e una lacuna dell'abaco del capitello, evidente nel disegno del Dosio (Fig. 1), la cui rottura fu forse causata dalla caduta della statua di Marc'Aurelio. Il Fontana risarciva il fusto con tasselli e grappe. Nei lavori, completati nel 1590, l'architetto erigeva le statue di S. Pietro e S. Paolo sugli attici delle Colonne. Rimodellava lo stilobate di base dell'Antonina, adattandolo all'interro di circa 6 metri (3) subìto dalla colonna nei secoli successivi la sua erezione, votata nel 175 d.C., e ne reintegrava il capitello (Fig. 2) ricostruendo l'angolo con i marmi cavati dal Settizonio.

Già dai primi sopralluoghi da noi eseguiti la presenza di lesioni in evoluzione in questi elementi d'angolo destò alcune preoccupazioni per la sua stabilità. L'analisi del quadro fessurativo evidenziò che le nuove lesioni avevano parzializzato gli inserti di marmo messi in opera nel 1590 alterando l'originario schema statico ideato da Fontana. Le rotture della pietra si erano innescate proprio in corrispondenza delle grappe metalliche poste in opera tra i blocchi. Tra le cause potevano addursi sia i fenomeni di dilatazione termica sia il rigonfiamento del metallo ossidato. Analoghi problemi di contatto tra marmo e inserti metallici erano riscontrabili alla Traiana. Qui i montanti della ringhiera infissi nel marmo avevano espulso i 4 angoli del capitello. Era evidente che le originali sigillature in piombo non erano state in grado nel corso dei secoli di preservare le sedi delle grappe dall'umidità e di assorbire le deformazioni del metallo durante le escursioni termiche. Tali inconvenienti hanno consigliato la sostituzione degli elementi metallici con altri in titanio e il ricorso allo stesso metallo per la realizzazione delle nuove strutture di sostegno. I vantaggi sono costituiti dalle caratteristiche di inalterabilità del titanio unitamente al suo coefficiente di dilatazione termica pressoché simile al marmo ($\alpha = 8{,}64 \mathrm{x} 10^{-6} \cong 7 \mathrm{x} 10^{-6}$) che rendono meno traumatico il contatto tra i due materiali.

Una precedente esperienza di cui si era a conoscenza nell' applicazione di questo metallo su monumenti, era costituita dalla messa in opera in Grecia di grappe di titanio sull' Eretteo e sul Partenone. Le nuove grappe sostituivano quelle in acciaio, messe in opera nella prima metà di questo secolo dal Balanos (4), intaccate in pochi anni dall'atmosfera inquinata di Atene.

Per la Colonna Antonina l'uso del titanio presentava maggiori incognite per le maggiori dimensioni degli elementi necessari per realizzare la carpenteria metallica della struttura di sostegno dell'angolo ricostruito del capitello. La sua progettazione ha preso avvio dalle ipotesi circa i criteri statici usati dal Fontana nella reintegrazione e sulla conformazione dei blocchi utilizzati. Una prima restituzione grafica fu eseguita in base alle linee di discontinuità visibili dall'esterno. Risultò che la lacuna venne reintegrata ponendo in opera tre grandi elementi marmorei. Il primo, a livello della fascia degli ovoli, è un cuneo incastrato a tutto spessore nel fusto fino al vano scala. La parte aggettante, che ricostruisce due ovoli completi, funge da appoggio ai due blocchi sovrastanti. Questi ultimi, affiancati all'incirca secondo la diagonale del capitello, ricostituiscono la parte mancante dell'abaco. I due blocchi trovano sostegno, oltre che sulla mensola sottostante, su seggiole di appoggio scavate nel marmo antico pressoché in corrispondenza degli assi del capitello. La parte aggettante dei due blocchi risultava svuotata superiormente e riempita da un massetto. Il lavoro di scalpellino per eseguire questo scavo risultò contabilizzato nel libro delle spese del cantiere (5) e quindi fu possibile valutarne a priori l'approfondimento. Nell'ipotesi di calcolo statico seguito dal Fontana l'alleggerimento delle estremità doveva servire a far cadere il baricentro degli inserti sulle seggiole d'appoggio. Inoltre la loro conformazione a coda di rondine impediva il ribaltamento delle mensole nelle delicate fasi di montaggio. Una serie di grappe metalliche aveva la funzione di semplice collegamento tra i vari conci dopo la loro posa in opera. L'originale integrità della pietra era infatti sufficiente a garantire la stabilità dell'angolo. La perdita di monoliticità dei mensoloni costituiva quindi una minaccia alla sicurezza dell'organismo strutturale ideato dal Fontana. Fu subito evidente la necessità di sostenere l'estremità, aggettante dagli ovoli, dei mensoloni superiori. Il progetto si orientò subito verso una struttura metallica a sbalzo dal fusto che, contenuta nel vuoto di alleggerimento superiore, agganciasse l'intradosso dell'abaco, in corrispondenza della bisettrice dell'angolo, impedendone così gli eventuali cinematismi di collasso.

La verifica della fattibilità del progetto richiedeva lo svuotamento dell'angolo e la rimozione di alcune grappe. Solo la conoscenza esatta delle soluzioni di continuità celate dal riempimento rendeva possibile la progettazione esecutiva della mensola in titanio e degli apparecchi di vincolo.

Tali operazioni richiesero la preventiva posa in opera di una struttura provvisoria di sostegno realizzata in acciaio zincato (Fig. 3). Ad un ottagono stretto alla base del peduccio della statua di S. Paolo venne agganciato, mediante un sistema di tiranti e puntoni, un traverso inferiore su cui era stato fatto poggiare, mediante martinetti a vite, l'intradosso dei mensoloni lapidei aggettanti dagli ovoli.

Si è quindi proceduto allo scavo del riempimento in malta pozzolanica dell'angolo, e alla rimozione della grappa obliqua che univa all'interno i due mensoloni e di quella esterna d'angolo. La rimozione delle grappe, causa delle lesioni più importanti visibili sui lati dell'abaco, ha permesso il riposizionamento dei vari frammenti e la bonifica della pietra mediante la cucitura delle soluzioni di continuità con resine e perni in ottone.

Sulla base del nuovo rilievo, che ha confermato le ipotesi formulate in precedenza, si è proceduto alla definizione della struttura definitiva.

L'apparecchio di sostegno individua una mensola vincolata mediante una cerniera in compressione ed un tirante, poi caricata da forze concentrate trasmesse da 4 pendoli. Il carico complessivo è stato valutato intorno alle 4 t, agenti con un braccio di circa 1 m dalla cerniera di appoggio.

La nuova struttura in titanio risulta essere composta da 3 pezzi principali: la mensola, la barra passante, e il capochiave interno alla scala. Forma e dimensioni sono state determinate più dalla disponibilità del titanio e dalle possibili lavorazioni che non dai risultati delle verifiche delle sezioni.
La mensola (l=1580 mm, h=400 mm) (Fig. 4) è stata ricavata da una lastra 2000x1000 mm, di spessore 20 mm. La forma rastremata

è stata dettata dalla necessità di ricavare dalla stessa lastra i pezzi necessari per realizzare il tacco di appoggio inferiore.

La barra (Fig. 5) è stata ottenuta dalla tornitura di un tondo Ø 57. L'originale progetto, che prevedeva una sezione Ø 60, fu abbandonato per la sparizione dell'attesa barra Ø 62 al suo arrivo a Roma.

Il capochiave (Fig. 6) è realizzato da una piastra di ripartizione ricurva, ricavata da una lastra s=10 mm, irrigidita da nervature saldate di s=20 mm. La possibilità di realizzare le saldature anziché bullonature come inizialmente previsto, fu verificata in secondo tempo dopo le prove di lavorazione.
Con la lastra da 10 mm sono state realizzate anche le 3 piastre di ripartizioni inferiori, collegate, mediante bulloni, ai pendoli che sostengono il marmo (6).

Come si può capire i maggiori problemi incontrati nella progettazione della carpenteria in titanio sono stati la limitata disponibilità dei pezzi di maggiori dimensioni e la mancanza di conoscenza, da parte di noi architetti e ingegneri civili, della tecnologia del titanio a cui si è potuto supplire solo dopo le prove di taglio, saldatura, foratura e tornitura eseguite in officina. Comunque anche la modellazione del marmo antico per accogliere il tacco di appoggio e l'esecuzione del foro passante per il tirante non hanno presentato minori difficoltà!

Eseguita la posa in opera del tirante, della mensola e del capochiave sono stati montati i pendolini e le sottostanti piastre di sostegno. Avvitandone i bulloni di fissaggio, a ciascun pendolo è stato imposto un pre-carico di circa 300 kg per recuperare le deformazioni dovute agli assestamenti iniziali. La tensione è stata controllata mediante strain-gauges i cui cavi di collegamento (Fig. 7) alla centralina di lettura sono stati fatti passare in un foro del fusto e fuoriuscire dalla piastra di partizione in modo da rendere possibili future letture di controllo sugli estensimetri lasciati in opera.

In corrispondenza dei punti di appoggio degli elementi in titanio con la pietra, la superficie è stata livellata con spessori di piombo. A questo è stato interposto un foglio di teflon a contatto del titanio.

La mensola in titanio è stata anche utilizzata per fissare 4 staffe superiori. A queste si aggancia il sistema di grappe studiato per contenere i vari frammenti delle sponde dei mensoloni (Fig. 8).

Anche per altre grappe antiche che presentavano problemi di corrosione si é proceduto alla sostituzione con elementi in titanio.

La nuova struttura, annegata in un nuovo riempimento in lapilli vulcanici e malta, è stata ricoperta da una lastra di marmo che ricostituisce il piano di calpestio. Sono rimaste in vista le piastre di sostegno inferiori (Figg. 9 e 10) praticamente invisibili all'altezza di "cento piedi" a cui si staglia la Colonna.

NOTE

(1) I lavori di restauro sono stati diretti dall'architetto Giangiacomo Martines, della Soprintendenza Archeologica.
Il gruppo di studio sui problemi statici era guidato dal Prof. Ing. Antonino Giuffré e ne facevano parte gli architetti Carlo Baggio e Fabio Ortolani con gli ingegneri Roberto Marnetto e Renato Masiani.

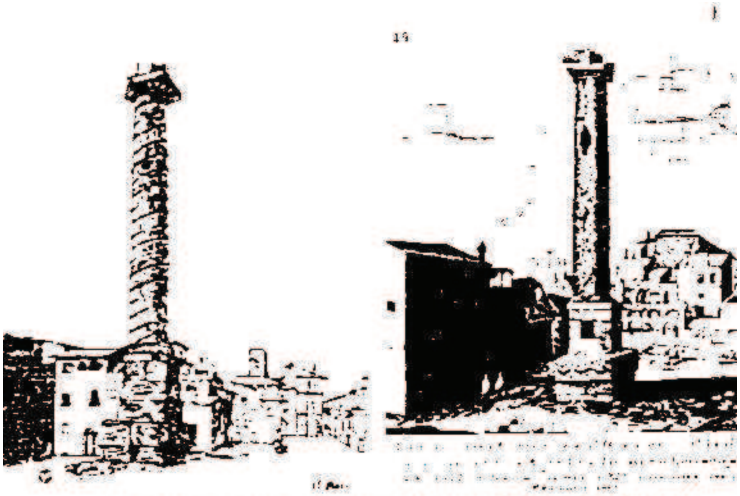
(2) A. Giuffré, F. Ortolani: Le Colonne Coclidi Testimoni dei Terremoti di Roma. "Tecnologia Scienza e Storia per la Conservazione del Costruito", pp. 99-118. Annali del Dipartimento di Costruzioni dell'Università di Firenze, Marzo-Giugno 1988.

(3) G. Lugli: Come si é trasformato il suolo di Roma.
Rendiconti dell'Accademia dei Lincei, s. VII, VI, pp. 477-491. Roma 1951.

(4) Th. Skoulikidis, N. Beloyiannis, E. Papakostantinou, D. Charalambous: Study for the Restoration of The Partenon. Appendice A: Type of Corrosion. Measures to be taken, pp. 73-76. Ministry of Culture and Sciences, Committee for the Preservation of Acropolis Monument. Athens 1983.

(5) Libro di Tutta la Spesa Fatta da N.S. Papa Sisto V alla Colonna Antonina e Traiana. Archivio Segreto Vaticano, Arch. Arcis Armario B3. Trascrizione a cura di O. Sforza e M.V. Zaccheo per la Soprintendenza Archeologica di Roma, Aprile 1984.

(6) La lastra da 10 mm é stata messa a disposizione dall'Istituto Centrale del Restauro. La lastra da 20mm è stata fornita dalla SEIPI di Milano che l'ha reperita in Gran Bretagna con conseguenti problemi sui tempi di consegna. Meno problematica è stata la fornitura dei restanti pezzi curata dalla GINATTA. Il titanio utilizzato é del tipo denominato Commercially Pure - Grade 2.



[illegible] (metà del sec.XVI) e [illegible]

COLONNA ANTONINA: G.B.Piranesi, 1760. Disegno ispirato dalla

Fig. 1 - Disegno di A. Dosio (metà del sec. XVI) in cui è visibile l'angolo sbrecciato del capitello della Colonna Antonina reintegrato da Domenico Fontana in occasione dei lavori di restauro e consolidamento conclusi nel 1590.

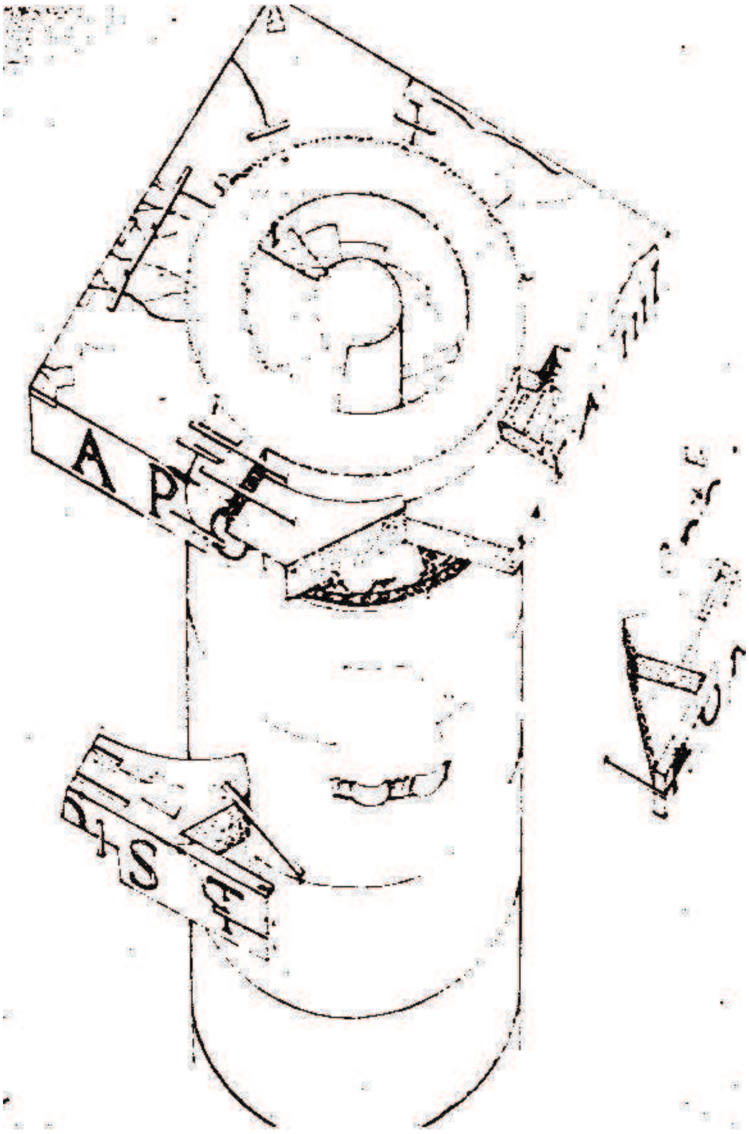


Fig. 2 - Rilievo del capitello con evidenziati gli inserti marmorei posti in opera da Fontana. Sono visibili le lesioni passanti in corrispondenza delle grappe d'angolo.

Fig. 3 - Struttura provvisoria in acciaio per sostenere i mensoloni durante le fasi di rimozione del massetto di riempimento dello scavo di alleggerimento superiore, di smontaggio delle grappe e di bonifica delle sponde frammentate.

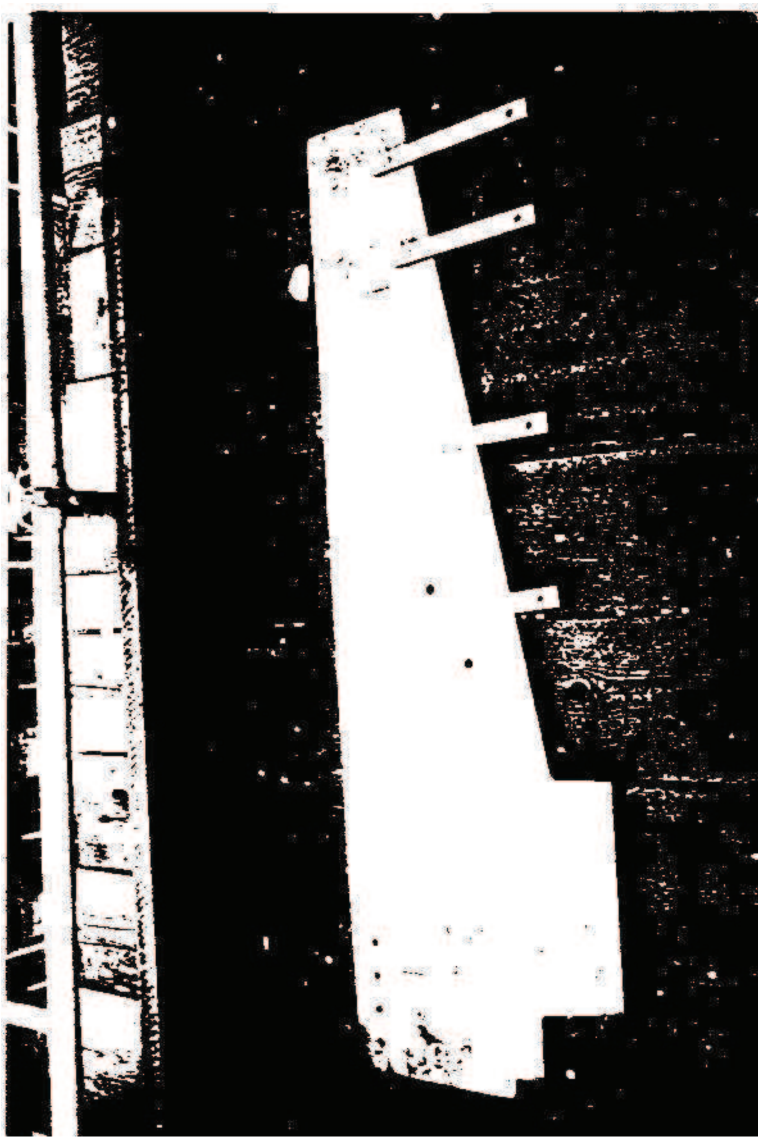


Fig. 4 - La mensola sul ponteggio prima della sua posa in opera. Sono montati gli agganci dei pendolini di sostegno inferiori; sono visibili i 4 fori per i perni di fissaggio del tirante superiore e in basso l'intonaco per l'apparecchio di appoggio, costituito da un angolare di titanio alloggiato nel marmo.

Fig. 5 - La barra, che costituisce il tirante superiore della mensola, vista fuori opera. E’ visibile la filettatura per il fissaggio del capochiave.

Fig. 6 - Capochiave realizzato da piastra ricurva

Fig. 7 - La mensola posta in opera. I cavi collegano gli “strain gages” posti sui pendolini per controllare i valori di pre-carico imposti alla struttura, alla centralina di lettura all’interno della Colonna.

Fig. 8 - Sistema di grappe in titanio

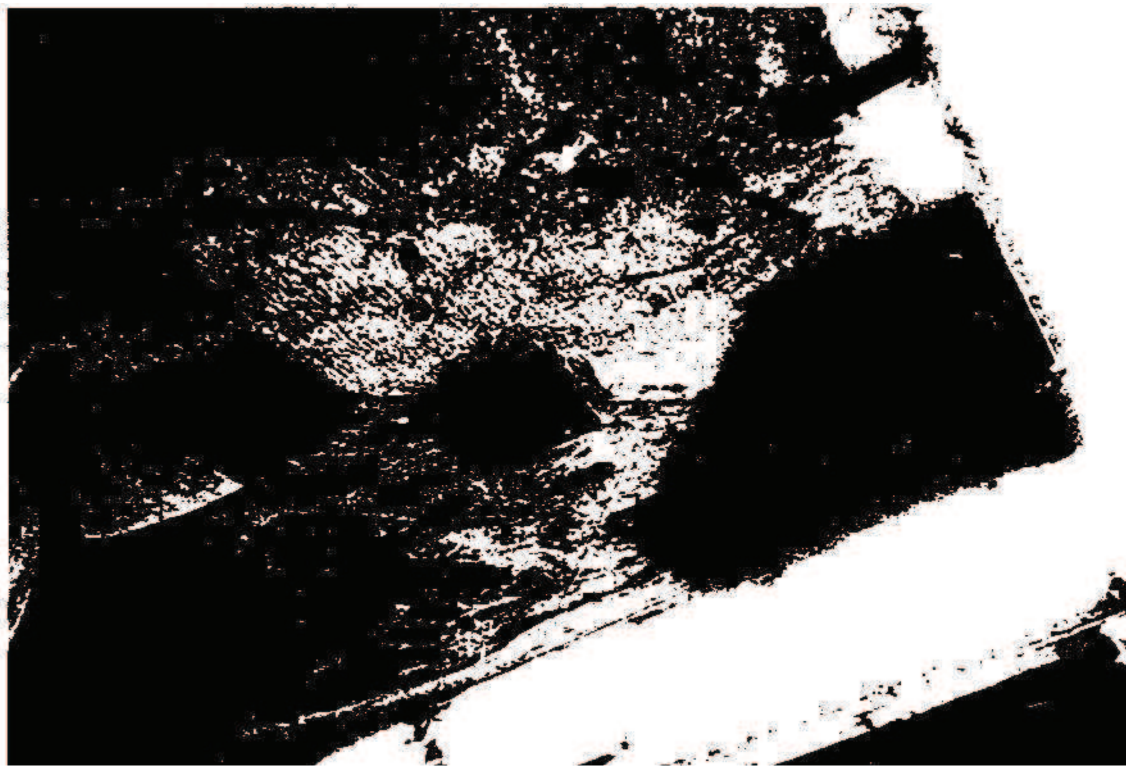


Fig. 9 - Piastre di sostegno inferiori

Fig. 10 - Vista dal basso delle piastre di sostegno inferiori

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NUMERICAL SIMULATION OF THE ALPHA CASE AS A QUALITY CRITERION FOR THE INVESTMENT CASTING OF SMALL, THIN-WALLED TITANIUM PARTS

SUMMARY

As yet, no casting and solidification process put forward for the investment casting of titanium allows castings to be produced without a hardness increase in the surface zone. Casting quality depends to a not insignificant extent on the structure of this surface zone. For these reasons, the alpha case was selected as a quality criterion.

On the basis of the diffusion kinetics of the alpha case components, a criterion function using simulation and modelling techniques to predict the alpha case quality criterion was developed. Calculations were compared with experimental results for the titanium casting and solidification process developed at the Institute, and iteratively optimized.

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1 - THE ALPHA CASE - WHAT IS IT - HOW AND WHY DOES IT FORM?

The selection of the mould material is an important consideration when casting reactive metals (1,2,3,4,6). Reduction of most refractory oxides by molten titanium produces reaction zones rich in oxygen, and known as the alpha case (fig. 1) (4,5,6). In addition to combining with titanium to form oxides in the film or scale, oxygen may also dissolve in the titanium interstitially, to the extent of more than 10% wt. Interstitially-dissolved oxygen tends to stabilize the alpha (hcp) phase of titanium. One of the prominent features of oxygen-contaminated material is therefore an alpha-stabilized surface zone immediately below the oxide scale (7,8,9).

The resulting "case" formed at the mould-metal interface is a material discontinuity, which normally has to be removed owing to its characteristically high-hardness inner scale. X-ray diffraction studies reveal an expanded c/a ratio in the inner scale.

The thickness of the layer increases with the time during which a high temperature is maintained in the mould-metal interface, limiting application of high mould pre-heat temperatures to thin sections. The depth of contamination is dependent on the section, with thick walls favouring greater penetration.

Surface contamination of this type may result in reduced tensile strength, flexural strength and fatigue strength, and severely affect susceptibility to stress-corrosion cracking (5,7).

Removal of the case poses problems on complex castings with varying section size.

Wax pattern tooling also has to be engineered for both the conventional casting allowance of the alloy and an extra acid metal removal allowance to permit removal of the metal-mould reaction layer. All wax patterns and as-cast parts are therefore slightly oversize, final tolerances being achieved only in the acid cleaning operation (6,7).

2 - CORRELATION BETWEEN ALPHA CASE AND CASTING PROPERTIES

Tensile strength is slightly higher and strain considerably higher in non-alpha-case as opposed to alpha-case specimens of the same material. As well as reducing ductility, the alpha case may be a contributing factor in stress crack propagation. Alpha-case castings possess only extremely low fatigue limits as compared to chemically milled castings. Hot isostatic pressing after chemical milling further enhances this advantage. The bending test also reveals a substantially lower bending angle for material with a brittle surface zone.

The high hardness of the surface zone could, however, result in certain advantages for components subjected to wear. A further not inconsiderable disadvantage as opposed, for example, to steel investment casting, lies in the generally inferior accuracy to size of investment-cast titanium, owing to differential alpha case formation and the resulting differential removal rates when the alpha case is eliminated.

3 - EXPERIMENTAL PROCEDURE

3.1 - Overview

In view of the above observations, the alpha case can be used as a measure of casting quality, insofar as appropriate quality values are defined for given depths of hardness penetration. A simple example, simultaneously acting as a "checking-device" is a casting wedge (Fig. 2). The influence of the mould material, casting and mould pre-heat temperatures and, especially in the case of the casting wedge, the geometrical influence on the extent of surface zone hardening are all relatively easy to determine. Alpha-case wedges integrally cast with the part can show whether post-processing by means of chemical milling has succeeded in removing the case completely.

3.2 - Casting the Alpha-case wedge

Fabrication of the investment mould is by the lost wax process, with application of the ceramic front layer to the wax model cluster using the investment casting shell mould technique (Fig. 3). The compacting method is used to introduce the backfill as a supporting material, for example in the case of conventional packaging for jewellery casting. De-waxing and firing are carried out in conventional furnaces.

Casting of the moulds takes place in a vacuum high-frequency induction spinning machine designed for relatively small melt masses, max 400 g (Fig. 4).

3.3 - Correlation between Alpha-case formation and process parameters

The influence of process parameters on the formation of the alpha case for centrifugal investment casting of titanium of small, thin-walled parts was investigated at the Foundry Institute.

After casting, the casting wedge was removed in such a way that the extent of surface zone hardening could be determined in relation to wall thickness (Fig. 5).

A comparison between the hardness distribution (measuring points with fitted curve) and the micrograph (vertical broken line) shows that the extent of alpha-case formation can be determined by either method. The left-hand diagram in Fig. 5 shows the thickness of the layer in a thinner-walled section of the wedge, the right-hand diagram the equivalent value for the thickest-walled section. There is less alpha-case formation in thinner sections.

The influence of the process parameters on formation of the alpha case is indicated below. The following significant influencing variables were investigated:

1. Mould pre-heat temperature;
2. Casting temperature;
3. Position of the casting in the mould;
4. Moment of acceleration in the centrifugal casting process.

Fig. 6 indicates the influence of mould pre-heat temperature and casting temperature on formation of the layer. Increased temperatures lead to greater surface brittleness.

The effects of the casting position in the mould and the filling rate of the mould cavity, shown here as functions of the moment of acceleration of the spinning machine arm, are demonstrated in Fig. 7. It will be evident that melt admission conditions during filling also play a role.

4 - NUMERICAL SIMULATION AS A TOOL FOR CASTING OPTIMIZATION

As well as meeting extreme strength requirements, highly-stressed titanium investment castings must increasingly conform to the highest accuracy-to-size-specifications, comparable for example with those for investment-cast steel parts. These two demands can be met only if the exact extent of the unavoidable alpha-case layer of titanium castings is known, and the layer can be removed with corresponding precision.

Prediction of alpha-case thickness is therefore helpful, and computer simulation offers a possible method.

Using a FEM programme, both the process parameters and the alpha-case thickness can be predicted.

The component geometry and the thermophysical and thermodynamic data (Diagram 1) of the casting metal and mould material are entered in the computer programme. The part in then meshed on the finite element principle (Fig. 8) and the thermophysical data calculated in accordance with the temperature distribution or cooling curves (Fig. 9).

Using criterion functions, the hardened layer can then be calculated from the temperature curves (Fig. 10). The criterion functions take account of the various influences of the process parameters and part geometry on the formation of the layer.

As already noted, the programme simultaneously enables, for example, temperature curves in the casting to be visualized. By modifying the simulated process parameters and ingate and feeder system, the user can perform a "cold cast". Time consuming and cost-intensive test series are shortened or eliminated.

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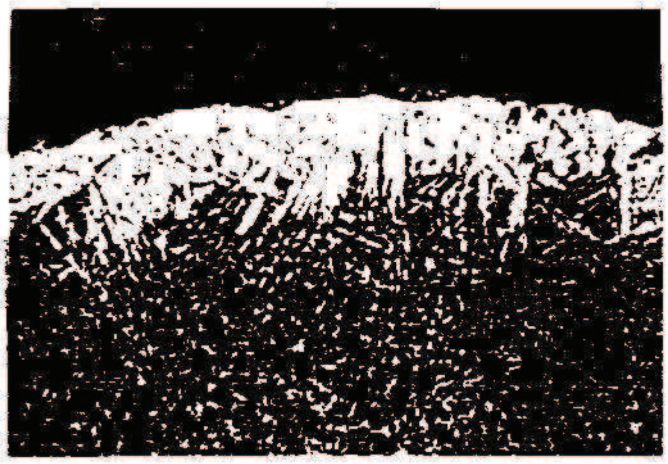

Fig. 1 - Commercially pure titanium with 0.3% Oxygen. The light margin represents the so-called alpha case

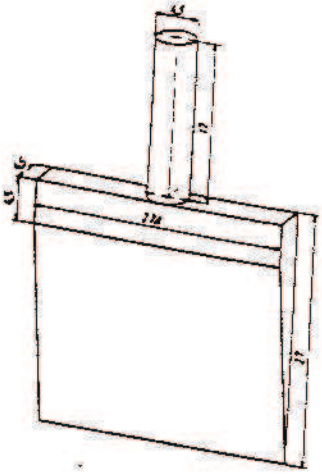

Fig. 2 - Casting wedge used to investigate the relationship between the extent of alpha

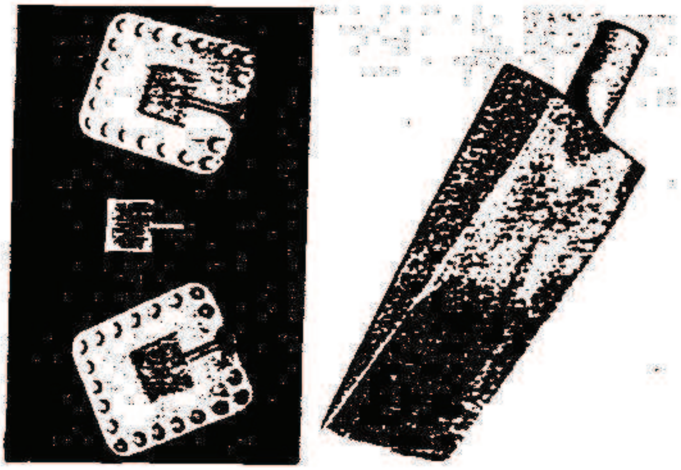

Fig. 3 - Investment casting method: injection mould, wax pattern, cast specimen

Fig. 4 - High frequency induction centrifuge caster (by courtesy of Linn Elektronik, Federal Republic of Germany)

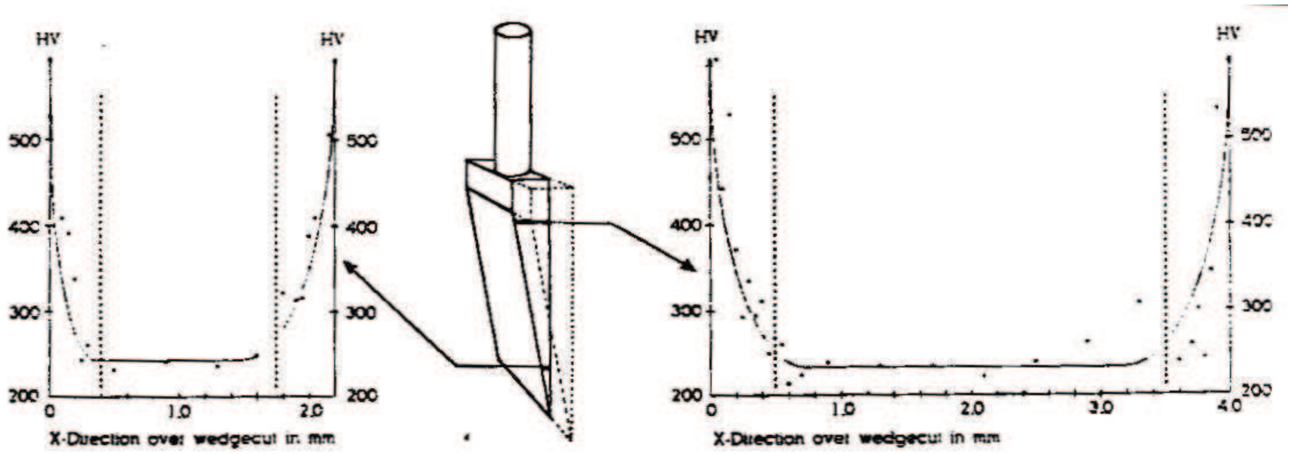

Fig. 5 - Alpha-case development and location in casting wedge. Right: deeper penetration due to thicker section; left: opposite effect

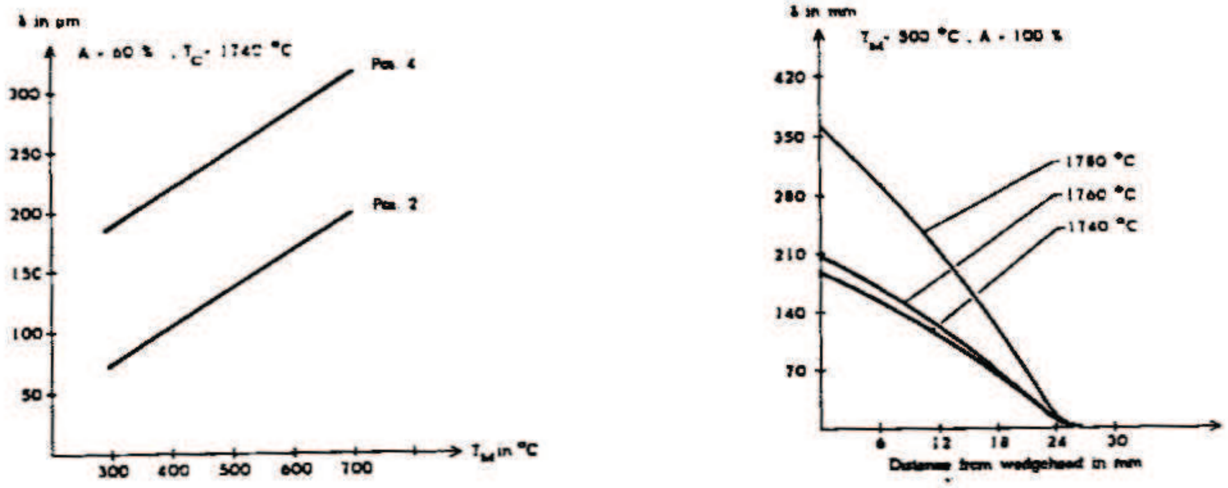

Fig. 6 - Alpha-case as a function of mould Pre-heating temperature (left) and casting temperature (right) at a defined point in the casting wedge

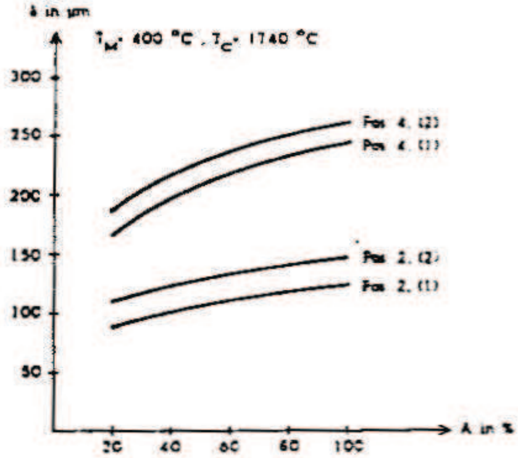

Fig. 7 - Layer thickness is also dependent on melt admission conditions in the mould. The figure shows the dependence of layer thickness on the investment mould acceleration moment at top (1) and bottom (2) of the wedge

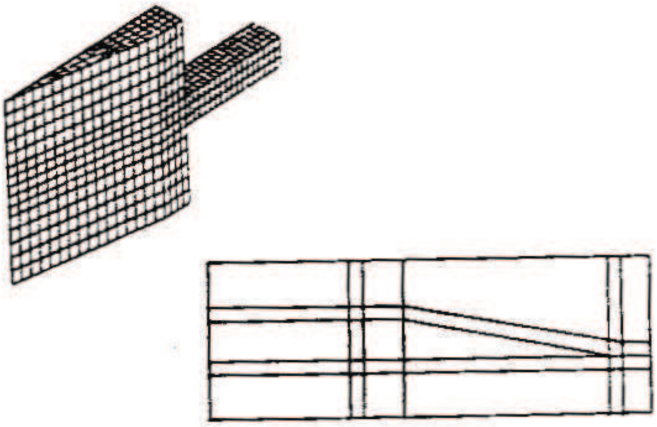

Fig. 8 - Meshing for FEM simulation

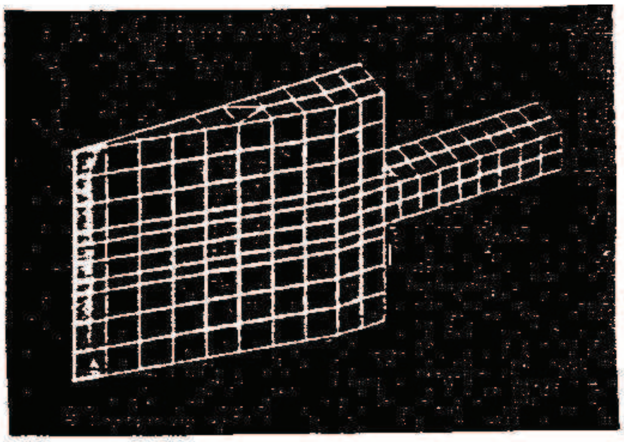

Fig. 9 - Using the CASTS programme package produced at the Institute, temperature distribution for any desired time increment can be calculated

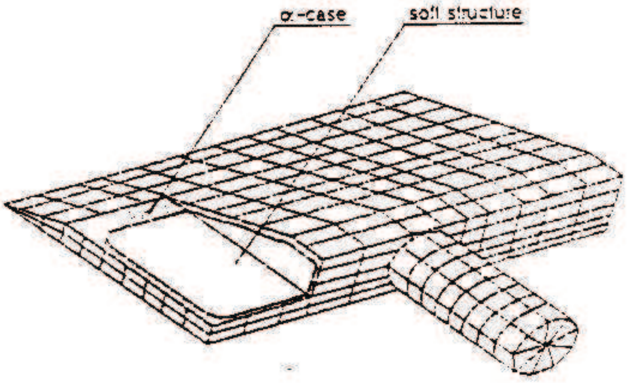

Fig. 10 - The thickness of the alpha-case layer can be visualized for any desired section through the casting

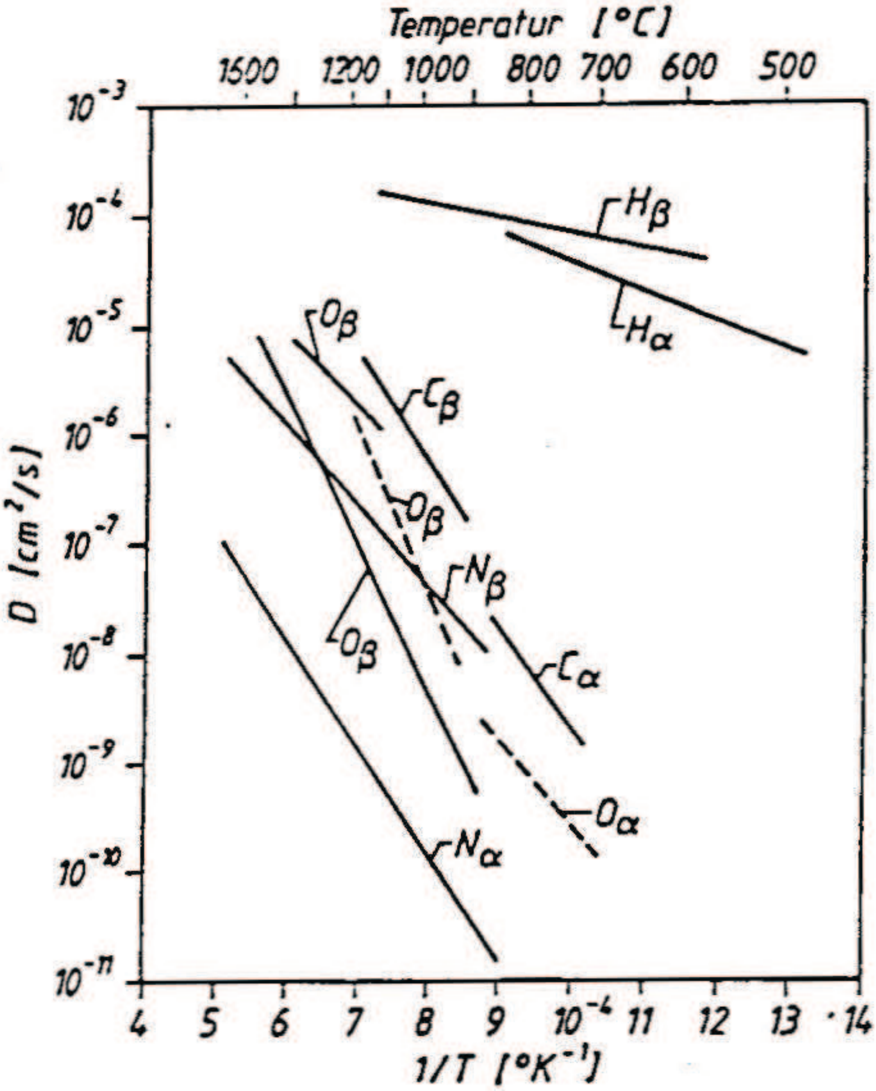

Diagram 1 - Diffusion of hydrogen, oxygen and nitrogen in alpha and beta titanium (9)

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TRATTAMENTO TERMICO IN FORNO A VUOTO DI GRANDI PARTICOLARI IN TITANIO (E LEGHE) PER APPLICAZIONI AERONAUTICHE.

1 - PREMESSA

Vengono descritti brevemente alcuni aspetti tecnici del trattamento termico in forno ad alto vuoto per particolari di Ti e Ti-Alloys di grande dimensione, indicando le procedure ed i requisiti generali di qualità per impieghi in campo aerospaziale.

Tali componenti vengono usati nelle applicazioni più critiche e devono raggiungere caratteristiche elevate nelle proprietà meccaniche e metallurgiche assicurando la loro integrità strutturale.

Il trattamento termico gioca un ruolo vitale in questa tecnologia.
Il ciclo termico viene eseguito sotto severe condizioni di controllo per evitare lacune nelle caratteristiche e verificare altresì che sia assicurata conformità alle specifiche.
Temperatura e livelli di (vuoto/gas parziali) pressione sono usualmente controllati con continuità da sofisticate apparecchiature digitali.

Coautori
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E' consuetudine eseguire il trattamento in accordo con la specifica MIL-H-81200.
L' operatività, la manutenzione del forno ed i relativi controlli pirometrici seguono le procedure previste dalla AMS 2750 (Aerospace Material Specification).
La camera calda (hot zone) è verificata periodicamente con le procedure del National Bureau of Standards.

L'insieme di queste norme e ormai l'attitudine ad operare in condizioni di massima sicurezza, rendono praticamente obbligatorio l'impiego del forno in alto vuoto, quando i particolari abbiano superfici finite o semifinite (sovrametallo inferiore a 0.5 mm) poiché è intrinseca nel tipo di impianto la perfetta tenuta e quindi diventano controllabili la composizione dell'atmosfera residua ed i processi di interazione superficiale gas-metallo ed eliminati i problemi di contaminazione, spesso riscontrati nei T.T. in forni ad atmosfere controllate o in bagno di sale (atmosfere di H_2 non possono comunque venire usate per ricottura o distensione del titanio per pericolo di contaminazione).

Viene mostrata la veduta di un forno (Fig. 1) in alto vuoto MOD. TPH/C-1500 T.A.V. a carro estraibile, probabilmente l'impianto di maggiori dimensioni presso una ditta di trattamento conto terzi (VACUUM - Trezzano S/N).
L'impianto ha elevate caratteristiche che gli consentono cicli veloci, ripetibili, con assoluta uniformità termica sia nel riscaldamento che nel raffreddamento.
Le superfici (n. 6) radianti, in corrispondenza dei lati di un cubo (il volume utile è 1,5x1,5x1,5 m^3) sono alimentate e controllate separatamente ed è possibile effettuare una speciale taratura sul modello, diversificando le potenze specifiche in funzione delle superfici esposte, così da raggiungere condizioni isotermiche durante i transitori.
Un complesso dispositivo di schermi, pilotato automaticamente, consente la più efficace scelta di raffreddamento della carica,

indirizzando il flusso (gas Ar, p=0,8-6 bar abs) attraverso diverse vie così da minimizzare le distorsioni e mantenere i particolari nelle dimensioni di tolleranza.
Il forno è evacuato con un doppio gruppo pompante in parallelo, ciascuno costituito da pompa a diffusione a vapori d'olio autofrazionatrice di grande portata, da pompa booster a lobi tipo Roots e da una pompa primaria a pistone rotante.
Tali gruppi assicurano pressioni operative in campo 10^{-6} mbar.

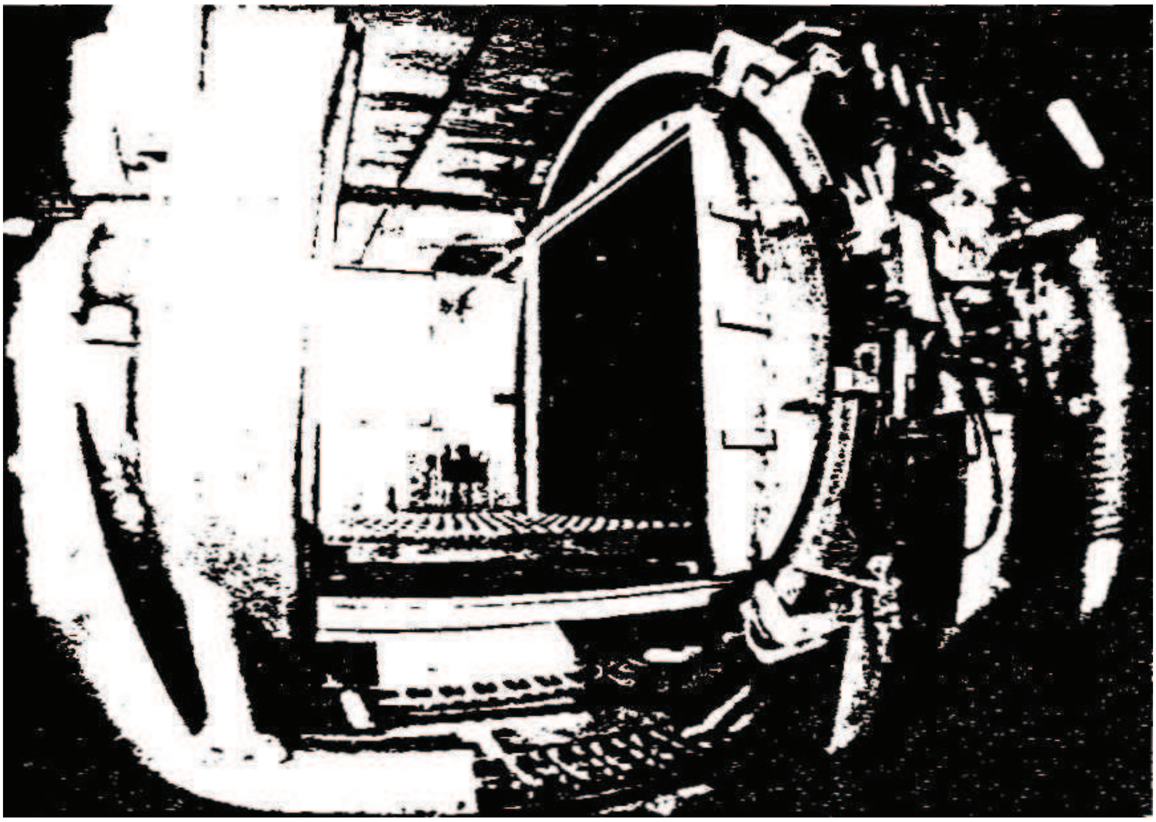


Fig. 1

2 - REQUISITI DI QUALITA'

Nella raccomandazione AIA-RQ-100 (Associazione Industrie Aerospaziali) vengono riassunti tutti gli aspetti qualitativi, comuni ai T.T., eseguiti su materiali metallici e componenti aerospaziali, e precisati i livelli di intervento della funzione qualità ditta (F.Q.D.) mediante i quali sia possibile assicurare che i requisiti tecnico qualitativi siano costantemente raggiunti e mantenuti.
Le NORME puntualizzano almeno i seguenti aspetti:

a) La precisione e la risoluzione dei dispositivi di misura e la frequenza delle verifiche ispettive.
b) I metodi di verifica dell'uniformità di temperatura.
c) Le procedure di esame dei risultati ottenuti dopo T.T. sul prodotto (prove di prestazione).
d) L'idoneità richiesta per il personale che opera nel settore dei T.T.

Per Ti e Ti-Alloys, la AIA-RQ-100 acquisisce la normativa MIL-H-81200 (mentre per gli acciai fa sua la MIL-H-6875).
Limitatamente alle termocoppie (classificazione e caratteristiche statiche) viene inglobata la UNI 7938 e la ANSI Me 96,1 (Tavole di conversione).

Relativamente alla classificazione e qualificazione degli impianti valgono rispettivamente le seguenti norme:

- MIL-F-80233 B (Furnaces, Vacuum, Heat treating integral quench) applicabile ai forni a vuoto a doppia camera con spegnimento in olio.

- MIL-F-80133 B (Furnaces, Vacuum, Heat treating and brazing) applicabile ai forni a vuoto a camera singola orizzontali (type I), verticali a caricamento dall'alto (type II) e verticali a suola sollevabile (type III).

- MIL-F-80258 (Furnaces, Heat treating, Electric, Natural atmosphere, Box Type) applicabile ai forni non a vuoto.

Gli impianti sono pertanto diversificati fra loro sulla base di vari fattori:

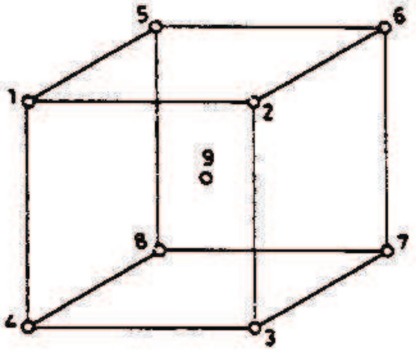
a) Tipo di costruzione, materiali usati, forma interna e/o esterna, tipo di apertura.
b) Mezzi di riscaldamento adoperati.
c) Fluidi usati (atmosfera/vuoto, bagni, ecc.) e loro movimentazione.
d) Dimensione della zona/e di lavoro.
e) Modalità operative (impianti batch/continui).

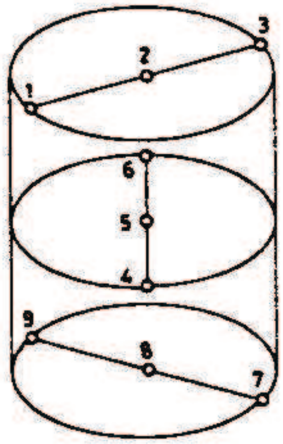
Nella Norma AIA-RQ-100 gli impianti sono classificati nella tabella IV.
In fase di qualificazione le principali operazioni di controllo richieste riguardano:

- verifica taratura strumenti di processo
- verifica uniformità temperatura nella "hot zone"
- verifica prestazioni tramite l'esecuzione di un processo di prova.

Di particolare rilevanza agli effetti della procedura di collaudo dell'impianto è il posizionamento delle termocoppie di prova.

Deve esservi una termocoppia ogni 0,7 m^3 di zona calda utile, con un minimo di 9 punti di misura ed un massimo di 40. La loro disposizione:





Ad ogni buon conto, è l'utente ad integrare con norme interne, normalmente più restrittive e complete, le specifiche di esercizio dell'impianto adattandole, caso per caso, alle proprie particolari esigenze.
Tali norme riguardano:

a) Cicli termici di prova (validi anche per la ricezione del forno) effettuati senza carico o con provette di vario materiale o con campioni di varia sagoma, misurando le velocità di variazione della temperatura in più punti sotto pressione parziale o in alto vuoto, con raffreddamenti in argon a varie pressioni con circolazione, a mezzo girante o senza, per verificare le performances dell'impianto.

b) Cicli di vuotamento e misurazioni di leak rate per la convalida della camera di vuoto e relativo gruppo di pompaggio. Le misure di leak sono richieste perché, pur con livelli di pressione inferiori a quelli limiti operativi (ottimi livelli di vuoto), (i normali controlli di vuoto non sono indicativi di piccole perdite) il titanio e le Ti-Alloys sono capaci di disciogliere l'ossigeno e l'azoto dell'aria, che penetrano nella camera attraverso una piccola fuga, anche se presenti in quantità minime, nella matrice metallica interstizialmente.

Tale contaminazione, che interessa prevalentemente lo strato superficiale, è sufficiente a determinare in un primo momento un indurimento della fase α e successivamente un infragilimento, che da innesco a cricche riducendo la resistenza a fatica del materiale ed abbassandone la resistenza alla corrosione.

c) Misure di retrodiffusione di vapori d'olio, che dissociandosi ad alta temperatura darebbero origine a picchi di H_2 e verrebbero assorbiti dal titanio.

Se si tiene conto che la ricottura in vuoto costituisce l'unico metodo pratico per rimuovere l'idrogeno interstiziale dal titanio, in condizioni di elevata retrodiffusione di idrocarburi, verrebbe a mancare la condizione primaria di trattamento.

Vengono pertanto richieste baffles criogeniche tra condotti di pompaggio e camera e verificati con spettrometri di massa a quadrupolo le concentrazioni di H_2.

d) Procedure di precleaning, per evitare contaminazione dei pezzi, che provochi infragilimento.

Tra le varie, citiamo quelle usate dal CERN per il titanio puro (e per la lega Ti-13V-11Cr-3Al) che attua i seguenti passaggi:

- rimozione delle tracce pesanti degli oli di lavorazione
- sgrassaggio (121°C) con vapori di percloroetilene
- lavaggio in bagno alcalino (pH = 11)
- risciacquo in acqua demineralizzata
- essicazione a 15°C in forno ad aria.

L'efficacia delle summenzionate procedure può essere verificata tramite analisi con spettrometria Auger.

e) Misure di velocità di riscaldamento e raffreddamento.
Misure di uniformità di temperatura nei transistori.

Mentre le norme si limitano a verificare situazioni di equilibrio termico in sistemi con cariche rarefatte (provini), è importante simulare le cariche reali per cercare di contenere la dispersione delle temperature nei transistori con opportune calibrazioni delle potenze irraggiate e con oculate sistemazioni della carica.
(Questo aspetto è tanto più importante con Ti e Ti-Alloys, in quanto le temperature in gioco sono più basse che con gli acciai, e più difficoltoso avviene lo scambio termico per irraggiamento).
A tal fine diventa rilevante il tipo di appoggio da dare alla carica stessa, la sua densità, la posizione relativa rispetto agli elementi riscaldanti ed alle bocche di flusso del gas di raffreddamento.

3 - TRATTAMENTO TERMICO DEL TITANIO E SUE LEGHE

3.1 - Considerazioni metallografiche

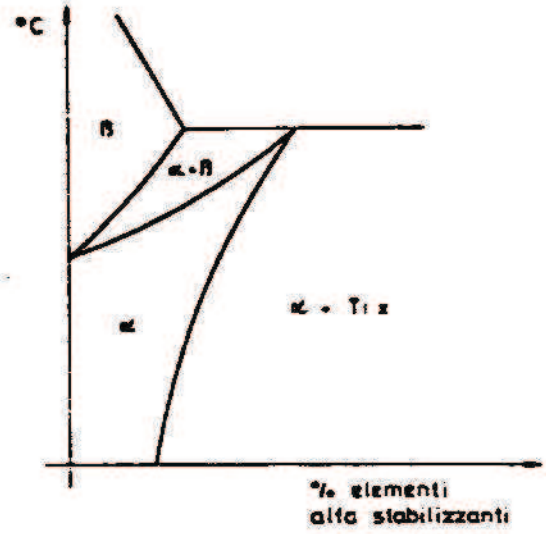
Il titanio ha una trasformazione allotropica $\alpha \leftrightarrow \beta$ a 885°C.
La struttura α è esagonale compatta, mentre quella β è cubica a corpo centrato.
Gli elementi di lega possono favorire l'una o l'altra struttura o essere anche neutri, per cui esistono leghe di tipo α, di tipo β e di tipo $\alpha + \beta$.

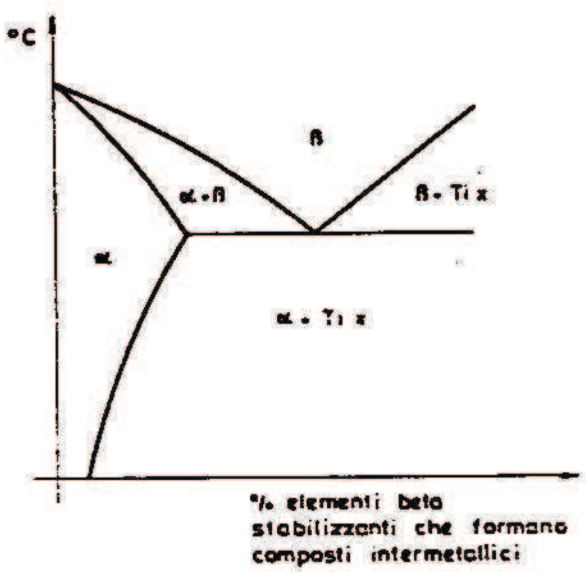
Sono elementi alfa stabilizzanti: C, O, N, Al, e Zr, i quali tendono a fare aumentare la temperatura critica di

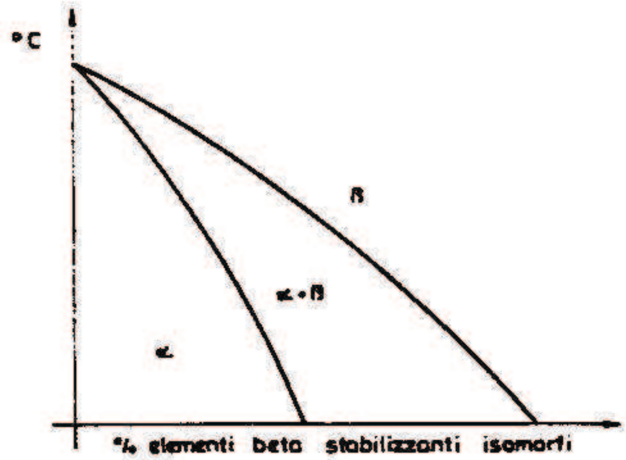
Trasformazione α ↔ β.

Sono elementi beta stabilizzanti: H, Mn, Cr, Mo, Fe, V e Cb che invece tendono ad abbassarla.

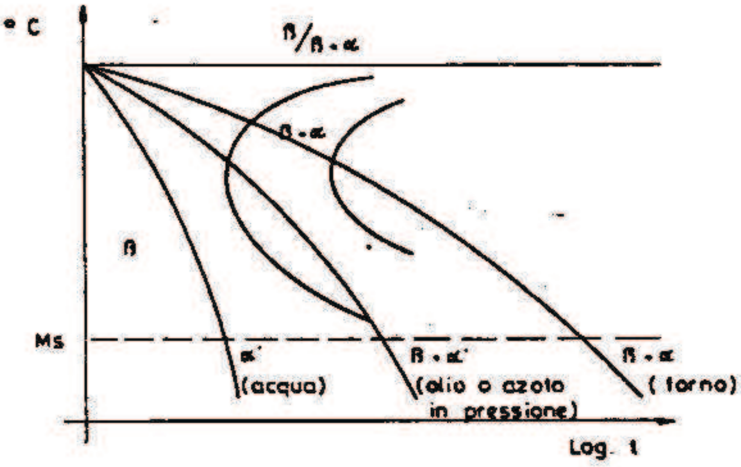
I diagrammi di stato tipici delle leghe di titanio possono essere sintetizzati dai diagrammi delle figure.







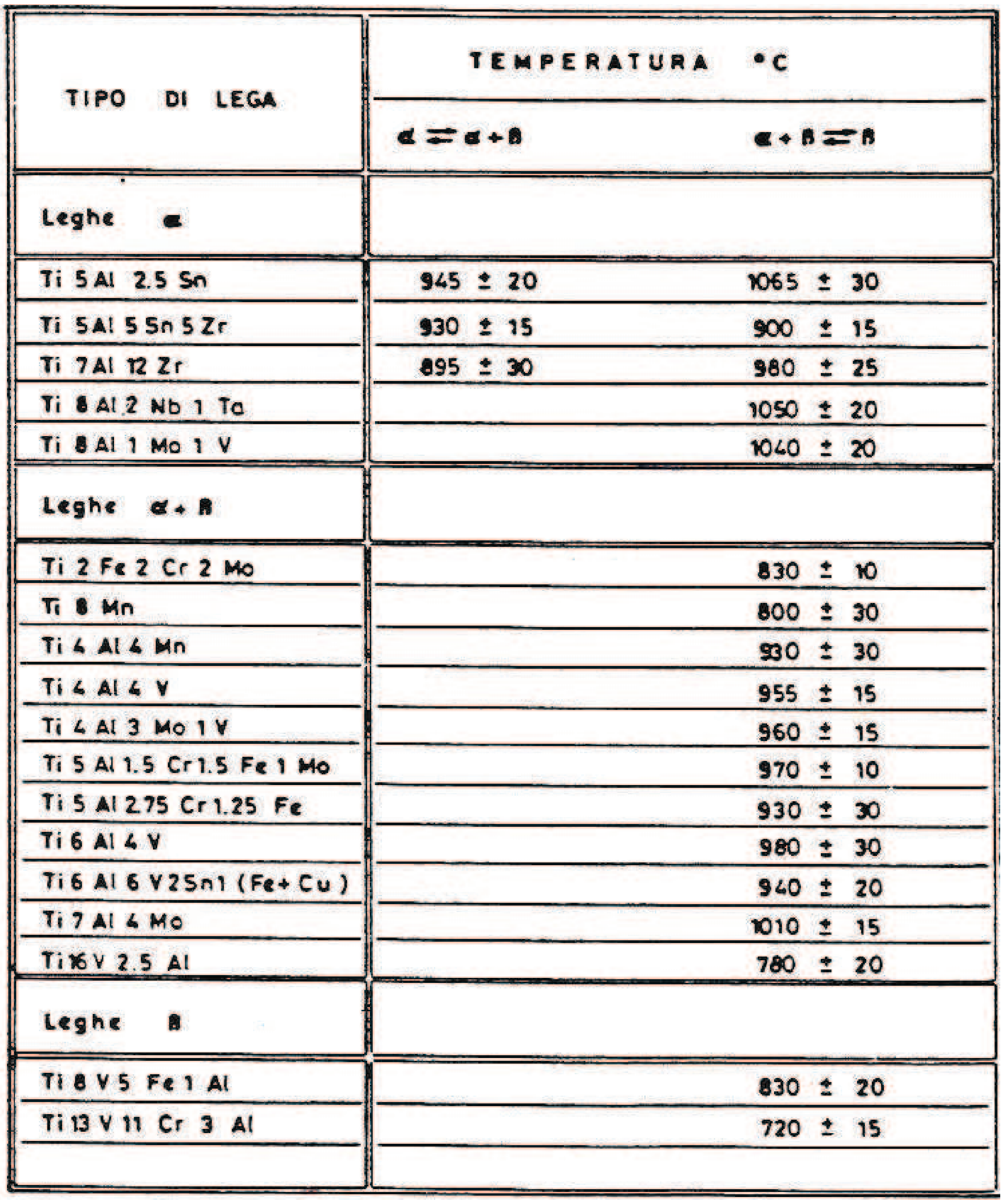
Anche per le leghe di titanio le trasformazioni allotropiche sono influenzate dalla velocità di raffreddamento come viene illustrato dal diagramma T.T.T.



Dal diagramma suddetto risulta come dopo aver riscaldato la lega nel campo Beta sia possibile ottenere una struttura di tipo martensitico denominata Alfa aciculare.

3.2 - Tipi di leghe di titanio

La tabella (qui descritta) riporta alcune leghe di titanio con relativa temperatura critica di trasformazione.



TIPO DI LEGA	TEMPERATURA °C	
	α ⇌ α + β	α + β ⇌ β
Leghe α		
Ti 5 Al 2.5 Sn	945 ± 20	1065 ± 30
Ti 5 Al 5 Sn 5 Zr	930 ± 15	900 ± 15
Ti 7 Al 12 Zr	895 ± 30	980 ± 25
Ti 8 Al 2 Nb 1 Ta		1050 ± 20
Ti 8 Al 1 Mo 1 V		1040 ± 20
Leghe α + β		
Ti 2 Fe 2 Cr 2 Mo		830 ± 10
Ti 8 Mn		800 ± 30
Ti 4 Al 4 Mn		930 ± 30
Ti 4 Al 4 V		955 ± 15
Ti 4 Al 3 Mo 1 V		960 ± 15
Ti 5 Al 1.5 Cr 1.5 Fe 1 Mo		970 ± 10
Ti 5 Al 2.75 Cr 1.25 Fe		930 ± 30
Ti 6 Al 4 V		980 ± 30
Ti 6 Al 6 V 2 Sn 1 (Fe + Cu)		940 ± 20
Ti 7 Al 4 Mo		1010 ± 15
Ti 16 V 2.5 Al		780 ± 20
Leghe β		
Ti 8 V 5 Fe 1 Al		830 ± 20
Ti 13 V 11 Cr 3 Al		720 ± 15

Le leghe α contengono sempre Al e sono presenti anche elementi beta stabilizzanti aggiunti per compensare le caratteristiche negative dell'Al con riferimento alla plasticità a caldo.

Non sono induribili mediante T.T.

Le leghe α + β contengono elementi beta stabilizzanti in % tali da fissare una % di costituente beta anche a temperatura ambiente.

Sono più resistenti, soprattutto a caldo, delle leghe α.

Sono suscettibili d'indurimento mediante trattamento di solubilizzazione e tempra e successiva precipitazione (invecchiamento).

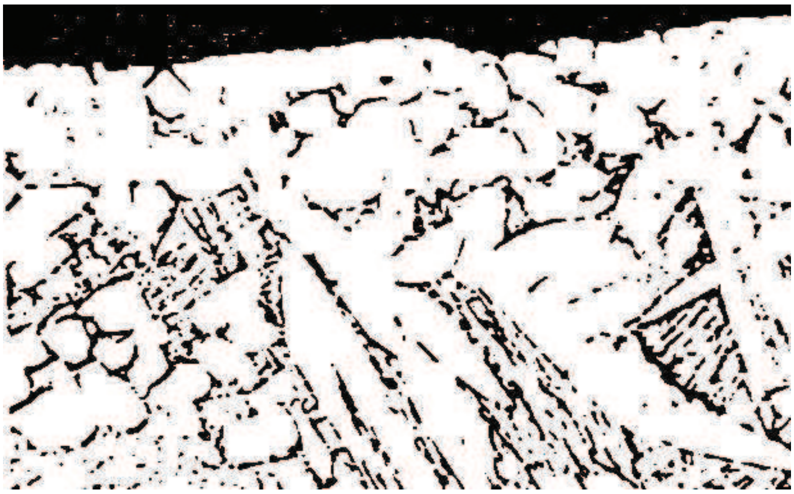
Le leghe β anche a temperatura ambiente sono costituite quasi completamente da fase beta metastabile.

Anche queste leghe sono induribili mediante trattamento di solubilizzazione e precipitazione.

3.3 - Interazione superficie - atmosfera

Le leghe di titanio sono fortemente suscettibili di contaminazione superficiale da ossigeno, idrogeno e da azoto.

L'ossigeno assorbito dopo esposizione in atmosfera ossidante a temperature superiori a 600-650°C, determina la formazione di uno strato di cristalli alfa (α) ricco di ossigeno caratterizzato da durezza più elevata ma molto fragile.



Tale strato riduce la resistenza a fatica degli organi meccanici a meno di non eseguire una asportazione meccanica successiva, essendo irreversibile tale processo di ossidazione.
Altra contaminazione altrettanto indesiderata è l'assorbimento di idrogeno che diffonde formando uno strato superficiale molto fragile caratterizzato metallograficamente dalla presenza di idruri quanto la % supera quella di max solubilità a quella temperatura.
Anche in questo caso si avrebbe una riduzione della resistenza a fatica dei pezzi.
L'idrogeno può essere assorbito o attraverso operazioni galvaniche di decapaggio o per contaminazione in fase di riscaldamento con atmosfere contenenti idrocarburi, idrogeno o vapor d'acqua.
Tale reazione però, è di tipo reversibile per cui l'idrogeno può essere facilmente eliminato riscaldando i pezzi in impianti a vuoto.
L'azoto diffonde nel titanio con maggiore difficoltà e tale fenomeno diventa apprezzabile dopo esposizione a temperature relativamente elevate (> 800°C) e per tempi prolungati. Infatti la nitrurazione delle leghe di titanio, molto richiesta nelle applicazioni in cui le caratteristiche antigrippanti del titanio la rendono necessaria, si esegue in bagni di sali fusi a temperature di circa 850°C o in forni a vuoto ottenendo profondità molto ridotte.

3.4 - Influenza delle modalità di trattamento sulle caratteristiche delle leghe di Ti

I trattamenti termici eseguiti sulle leghe di titanio sono la stabilizzazione o distensione, la ricottura e l'indurimento.

La distensione viene eseguita per eliminare o ridurre le tensioni createsi durante la fabbricazione senza influenzare le caratteristiche meccaniche di resistenza e consiste nel riscaldare i pezzi a temperature comprese tra 480°C e 700°C per durate variabili da pochi minuti ad alcune ore e raffreddandoli di solito lentamente.

La ricottura conferisce alle leghe di titanio elevate caratteristiche di tenacità e di lavorabilità nonché la massima stabilità dimensionale.
Il trattamento consiste nel riscaldare le leghe di titanio a temperature comprese nel campo α (per le leghe α), e nel campo $\alpha + \beta$ (per le leghe $\alpha + \beta$) per durate variabili da pochi minuti fino ad alcune ore con raffreddamento finale lento.
Le leghe β si riscaldano a temperature comprese nel campo β.
Le leghe a normalmente subiscono un doppio trattamento di ricottura per aumentare la resistenza allo scorrimento a caldo.
Il primo trattamento, che si può considerare una solubilizzazione, si eseguirà da una temperatura di 50°C inferiore alla temperatura critica $(\alpha + \beta) \leftrightarrow \beta$ per una breve durata.

L'indurimento delle leghe $(\alpha + \beta)$ e (β) eseguito per incrementare la resistenza meccanica consiste in una tempra di soluzione riscaldando i pezzi ad una temperatura compresa nel campo $(\alpha + \beta)$ o (β), nel raffreddarli velocemente e poi sottoponendoli a trattamento di invecchiamento.
La temperatura di solubilizzazione, da durata e le modalità di raffreddamento influenzano significativamente le caratteristiche meccaniche ottenibili, nonché le caratteristiche dimensionali dei pezzi stessi.
Per le leghe $(\alpha + \beta)$ i migliori risultati di resistenza alla rottura, allo snervamento, di tenacità e di duttilità si ottengono riscaldandole ad una temperatura

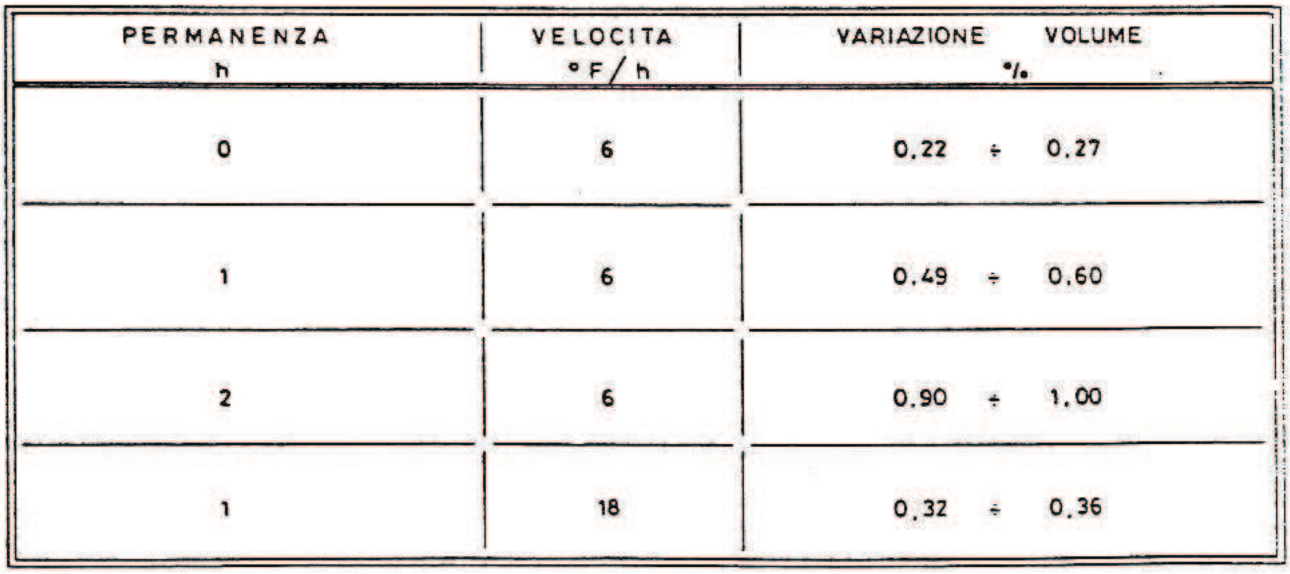
corrispondente al campo di transizione $(\alpha+\beta) \leftrightarrow \beta$ e raffreddandole velocemente; segue il trattamento di invecchiamento.

E' necessario pertanto determinare con precisione la temperatura di solubilizzazione e la velocità di raffreddamento ideale.

Il ricorso agli impianti a vuoto è particolarmente positivo per la loro nota affidabilità e quindi per la ripetibilità dei cicli di trattamento con riferimento sia alla precisione delle temperature scelte che alle modalità di raffreddamento ottenute facendo variare a piacimento la pressione del flusso d'azoto.

Con riferimento alle caratteristiche dimensionali, è stato dimostrato come, soprattutto per i pezzi di grandi dimensioni vi è un aumento di volume rilevato dopo trattamento e che è influenzato sia dalla temperatura che dalla velocità di riscaldamento. Tale aumento è tanto più marcato quanto più prolungata è la permanenza alla temperatura di solubilizzazione e quanto più il riscaldamento è lento.

Con riferimento a prove di trattamento di barrette in lega TiAl6V4 aventi diametro di 50 mm, appartenenti a due colate, sottoposte prima ad un trattamento di ricottura, sono state rilevate le seguenti variazioni - (Metals Handbook - 2° rd 1961):



PERMANENZA h	VELOCITA °F/h	VARIAZIONE VOLUME %
0	6	0.22 ÷ 0.27
1	6	0.49 ÷ 0.60
2	6	0.90 ÷ 1.00
1	18	0.32 ÷ 0.36

La temperatura di solubilizzazione era stata di 945°C mentre la temperatura di transizione dei campioni era di 988°C e 1015°C.

4 - TRATTAMENTO TERMICO DEI DISCHI ROTORE DELLA SEZIONE COMPRESSORE DI UNA TURBINA A GAS

Rappresentano uno dei casi più complessi di trattamento, trattandosi di particolari forgiati di grossa dimensione in lega: Ti-2Fe-2Cr-2Mo (lega $\alpha + \beta$) (Ti - 140A).

Nelle turbine a gas sono in lega di titanio anche gli stadi del compressore e gli anelli distanziali degli stadi, la protezione delle palette statoriche, la carcassa dei cuscinetti, lo schermo esterno dell'albero turbina.

Solo con un trattamento termico appropriato è possibile ottenere caratteristiche di duttilità (allungamento e strizione) come richieste da specifica.

Le condizioni iniziali del materiale sono quelle proprie di un materiale che ha subito una ricottura di distensione.

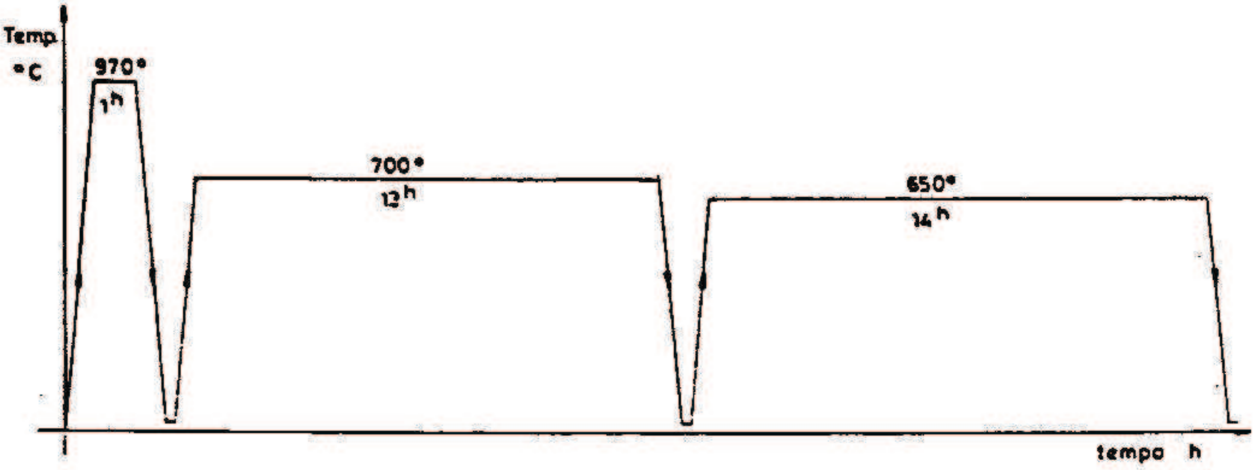
Il trattamento termico eseguito (Ti - 140A) è consistito in (Vedi schema ciclo termico):

a) solubilizzazione
riscaldamento fino a 970°C - permanenza 1 h - raffreddamento veloce

b) invecchiamento
riscaldamento fino a 700°C - permanenza 13 h - raffreddamento veloce

c) ricottura di stabilizzazione
riscaldamento fino a 650°C - permanenza 14 h - raffreddamento in aria.

Gli effetti di questo trattamento hanno quasi raddoppiato i valori di allungamento (25%) con una trascurabile variazione del carico a trazione da 112.5 kg/mm^2 a 109.0 kgf/mm^2.



Come già detto precedentemente, particolare cura è stata posta sulla scelta dei parametri di T.T.: velocità di riscaldo, temperatura di riscaldo e modalità di raffreddamento, perché ognuno influenza marcatamente le possibilità di ottenere le caratteristiche richieste, sono stati introdotti in un programma gestito dal PC a bordo impianto.
Le caratteristiche di vuoto (p.s. 1x10^{-5} mbar) hanno completamente eliminato i problemi relativi alla contaminazione superficiale.

5 - CONCLUSIONI

Sono state illustrate le caratteristiche impiantistiche di un forno a vuoto particolarmente attrezzato per il trattamento termico di organi realizzati in lega di titanio.

L'utilizzo di un impianto ad alto vuoto per il trattamento di queste leghe è da considerarsi "obbligato" a causa delle particolari esigenze richieste sia con riferimento alle caratteristiche superficiali rese particolarmente critiche dell'elevata reattività del titanio, che ai parametri del ciclo termico da attuare che influenzano significativamente sia le caratteristiche di resistenza, tenacità e duttilità che quelle dimensionali.

Thierry Roger
Extramet, France

MELTING AND UPGRADING OF TITANIUM POWDERS BY MEANS OF A HIGH FREQUENCY INDUCTIVELY COUPLED PLASMA

EXTRAMET is an indipendent Company whose main aim is applied research in extractive metallurgy; its principal fields of expertise are:

- Molten Salts Technology;
- Metallothermy;
- Hydrometallurgy;
- Oxides chlorination;
- Inductively coupled plasma technology

As far as inductively coupled plasma technology is concerned EXTRAMET is studying its applications to metals melting and refining and to metallic and ceramic powders elaboration.

The object of this presentation is to show some of the results obtained on melting and upgrading of titanium powders and thus the interest of the inductively coupled plasma in titanium metallurgy.

The process developed is included in a new route of production titanium (ingots or powders) from titanium tetrachloride;

The first stage consists of reduction of tetrachloride by a reactive metal in a molten salt bath. It results in a powder which undergoes a plasma treatment in order to meet the specifications.

The choice of inductively coupled plasma technology with this object is obvious because of its peculiar thermodynamical, energy transfer, chemical and hydrodynamical properties.
In the case of this application, the plasma is a thermal plasma obtained at atmospheric pressure.
Let us consider the most important properties of this type of plasma.

Figure 1 represents the enthalpy as a function of temperature for various plasma gases at atmosphere pressure. The steep variations of the enthalpy are essentially due to the heats of dissociation and ionization.

The very high enthalpy (and temperature) of the plasma and the possibility of transferring a large amount of energy to the plasma, independently in a large range of its nature, makes it very attractive for thermal treatments of refractory materials; thus, it is much more interesting than a flame, for example, because it permits storage and restitution, with a higher yield, of a large and controlled amount of energy.

The macroscopic transport of matter (diffusion), of charge (electrical conductivity) of momentum (viscosity) and of energy (thermal conductivity), in the plasma have to be considered in order to adapt the properties of plasma to the process.

Figure 2 represents the viscosity of argon, nitrogen, hydrogen and helium as a function of temperature. The viscosity of plasmas near 10.000 K lies in the range of 1×10^{-4} to 4×10^{-4} kg/m.s; these values are about 10 times higher than for the same gases at room temperature. One has to mention, as consequences, the difficulty of mixing gases or of introducing solid particles into some plasma areas and the importance of transfer between plasma and for example liquid metals.

The figure also shows the thermal conductivity of the same gases as a function of temperature. Its value, which depends strongly on the nature of the gas, is high; it is in the same order of magnitude as some metals.

Thus it is possible to produce plasmas with high values of viscosity and thermal conductivity and, therefore, to obtain very efficient thermal transfers between the plasma and the material.

Let us consider the peculiar properties of inductively coupled plasma (Fig. 3). These figures represent isovelocities and isotherms in a plasma generated in the torch schematized on the left. We observe the plasma peculiar configuration and the relatively low velocity of gas (comprised between 5 and 24 m/s). (In arc plasmas, velocities are in the range of several hundred m/s).

Therefore, the residence time of powders injected in this type of plasma is long.
Inductive plasmas are generated without electrodes which makes possible the use of reactive gases, and ultrapure material elaboration.

Let us say, for instance, the industrial application of this technology to the production of ultra-pure silica for optical fibres from technical tetrachloride.

These peculiar properties i.e. work at atmosphere pressure, low thermal inertia, its easy automation ... make of inductive plasma a choice tool for metallic and ceramic powders elaboration and transformation.

On Fig. 4 a 60 kW reactor is shown. The coil generates in that case an argon plasma.

In Fig. 5 we see the scheme of the setup used for titanium discontinuous melting. In this setup the material is placed in a water cooled crucible under the plasma.

The continuous treatment of titanium powder is realized in the setup of Fig. 6. In this case, the torch is composed of 3 quartz tubes.

An important purifying effect of the plasma has been observed in all our experiments. For example, analysis of a sample of titanium elaborated in the discontinuous reactor with an Argon-Helium plasma has given these results (Fig. 7). They show the effectiveness of the process to eliminate completely volatile impurities such as chlorine and sodium and reduce sensibly the amount of other impurities.

The process key parameters have been determined and classified. We have (Fig. 8), inter alia, studied the influence of plasma gas nature, raw materials quality, and the effect of a flux added to the raw materials.

For the study of the influence of raw materials quality on the process efficiency (Fig. 9), three kinds of materials have been used: microsponge, powder and turnings.
For instance, pellets composed of titanium powders and microsponge have been treated with an argon helium plasma.
These curves (Fig. 10) represent the eliminated % of a considered element as a function of microsponge % in pellets. Three dilution zones can be distinguished.
The first one (up to 30% microsponge in pellets) corresponds to a melted product, the second one (between 30 and 80 %) corresponds to a spongious product and the last one (from 80 to 100%) to a sintered product.
We clearly see that the maximum purifying effect is obtained at about 30% for a melted product.

We have compared the effect of two plasma gases on the purification of titanium, in identical thermal transfer conditions (Fig. 11).
In both cases a comparable quantity of impurities has been eliminated. In the case of Argon Hydrogen plasma the contents of H2 in the product is 99 ppm (lower than the tolerated quantity). Therefore an Ar-H_2 plasma can possibly be used.

We also studied the fluxes nature and quantity effect on titanium purification (Fig. 12). The fluxes tested have been fluorides of Li, Na, K, Ca, and Mg.
We see the interest of adding 1% of calcium fluoride and 0,5% of sodium fluoride to the raw materials for the elimination of impurities such as iron.

A strategy of characterization has been defined. All the methods used give information a posteriori, even if some of them allow appreciation the material properties and of the importance of the transfers during the treatment. In order to follow up the melting and purification of the metal in situ, a method which uses emission spectroscopy of elements has been carried out. The experimental setup (Fig. 13) is comprised of an optical fibre, a spectrometer and an optical multichannel analyser.

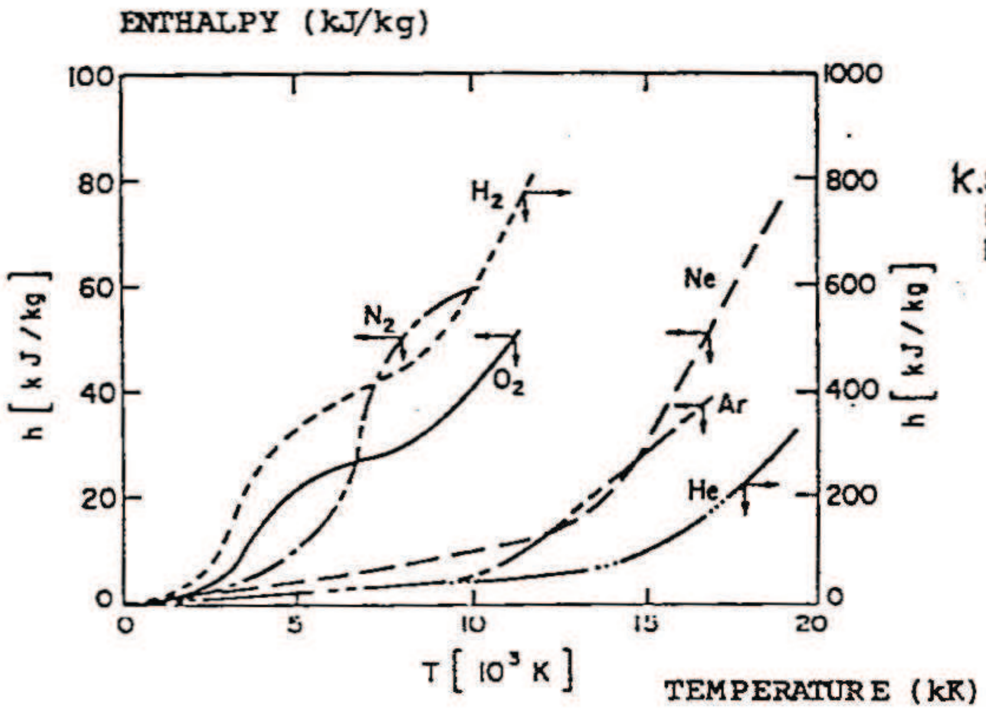
We have shown that the main purification phenomenon is evaporation of impurities in elementary or molecular form according to their physical and chemical properties.

A correlation of the impurities eliminated percentage (determined by analysis) and the surface under the curve of their emission intensity in the plasma as a function of time has been established (Fig. 14). As a result, the control of the process can be achieved. We also verify the best effect of potassium fluoride on titanium purification.

Thus, we have studied:

- the key parameters influence on process efficiency
- the chemical transfers at plasma-material interface
- the thermal transfers
- the process control.

The objective of future development of this process includes its optimization and its scale up to industrial production.
Production capacities of about 70 t/y are considered a first development step.



Ref.:
K.S. Drellishak,
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Northerwestern
University,
Evanston, IL,
1963

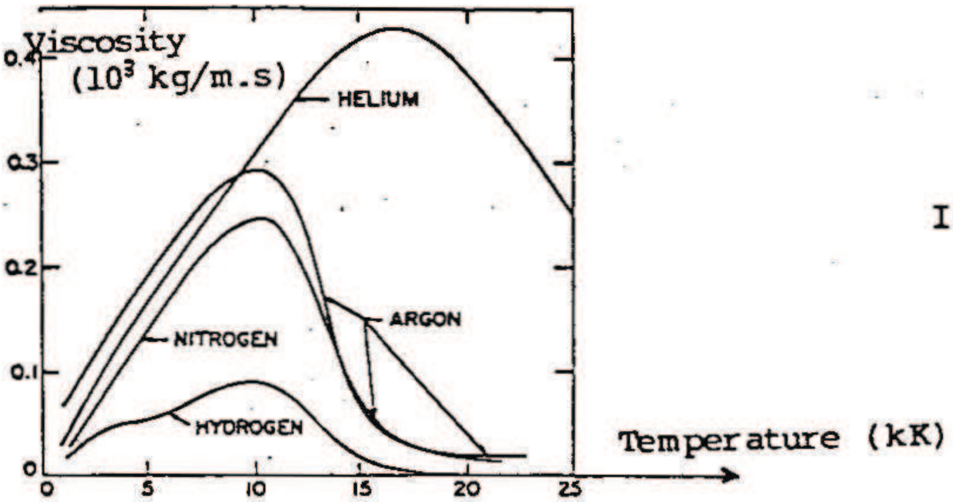
- Very High Enthalpy

- Enthalpy obtained from an outer source of energy

-> Transfer to materials of a very large and controlled amount of energy with a high yield

Fig. 1 - Enthalpy of a thermal plasma

TRANSPORT OF
- Matter (Diffusion)
- Charge (Electrical Conductivity)
- Momentum (viscosity)
- Energy (Thermal Conductivity)



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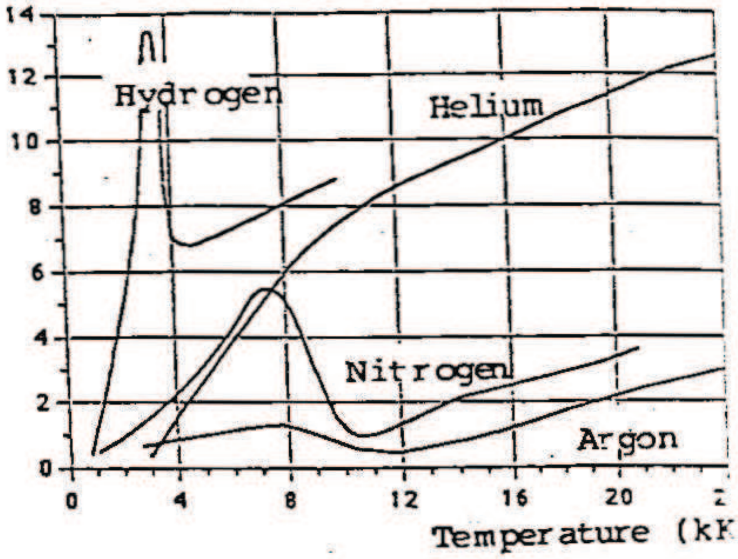

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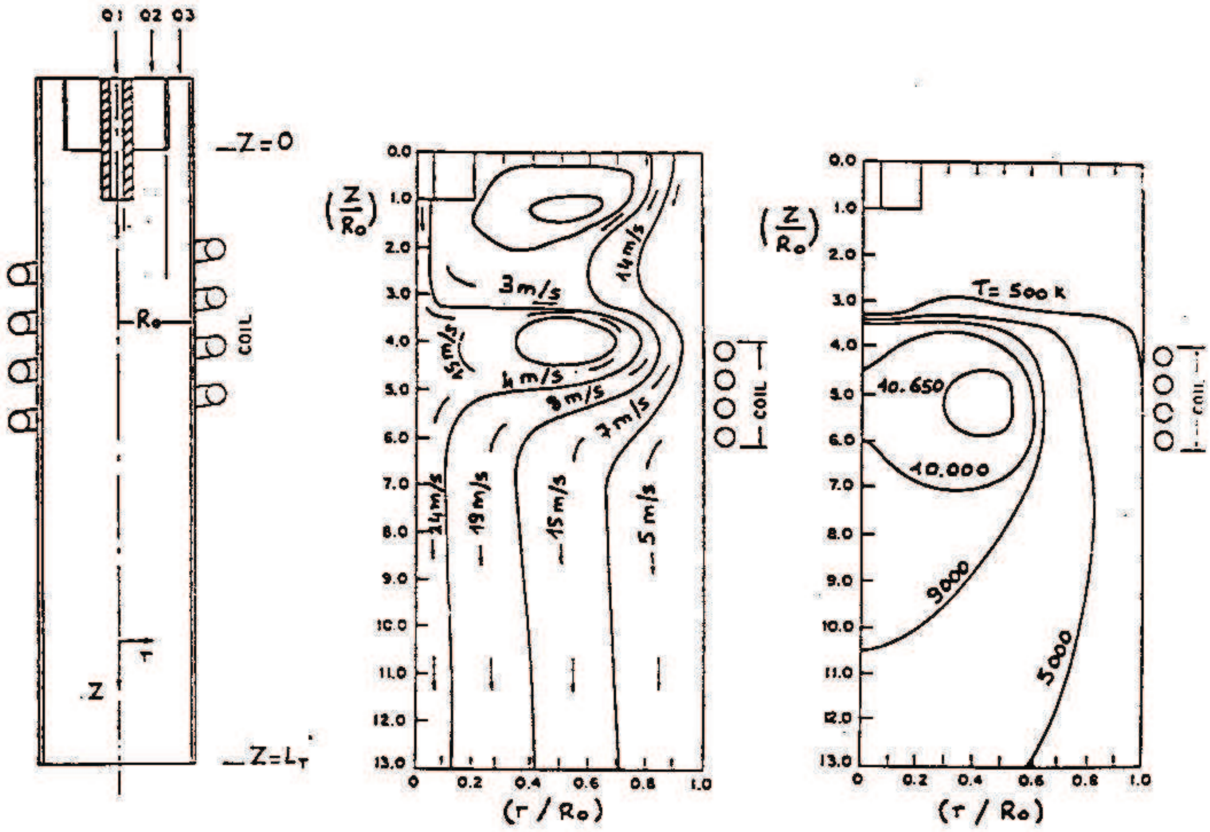
Actualité
chimique,
Dec.1981, 10,
pp 15-36

High Viscosity → Efficient Plasma-Material Thermal Transfer

High Thermal Conductivity → Efficient Plasma-Material Thermal Transfer

Fig. 2 - Transport properties of thermal plasma

FLOW AND TEMPERATURE FIELDS IN THE DISCHARGE REGIONS



(Q1;Q2;Q3 = 0.4;2.0;16 l/mn - LT = 18.2 cm
Ro = 1.4 cm - f = 3 MHz - P = 3.77 kW)

Ref.: M.I. Boulos; IEEE, Trans, Pl. Sc., PS-6, 93, 1978

- Peculiar Configuration
- Low Velocity Gas

ELECTRODELESS PLASMA

- Possibility of Using Reactive Gas
- High Purity Level

Fig. 3 - Characteristics of inductively coupled thermal plasma

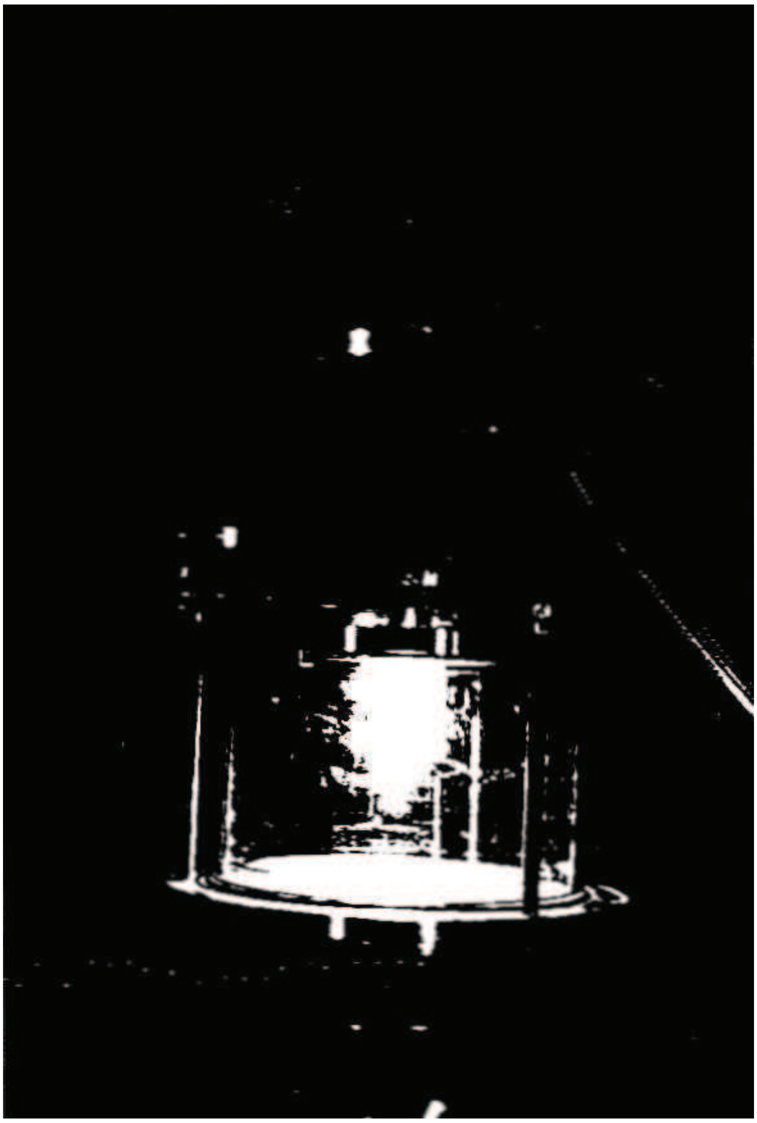


Fig. 4 - The 60 kW plasma reactor

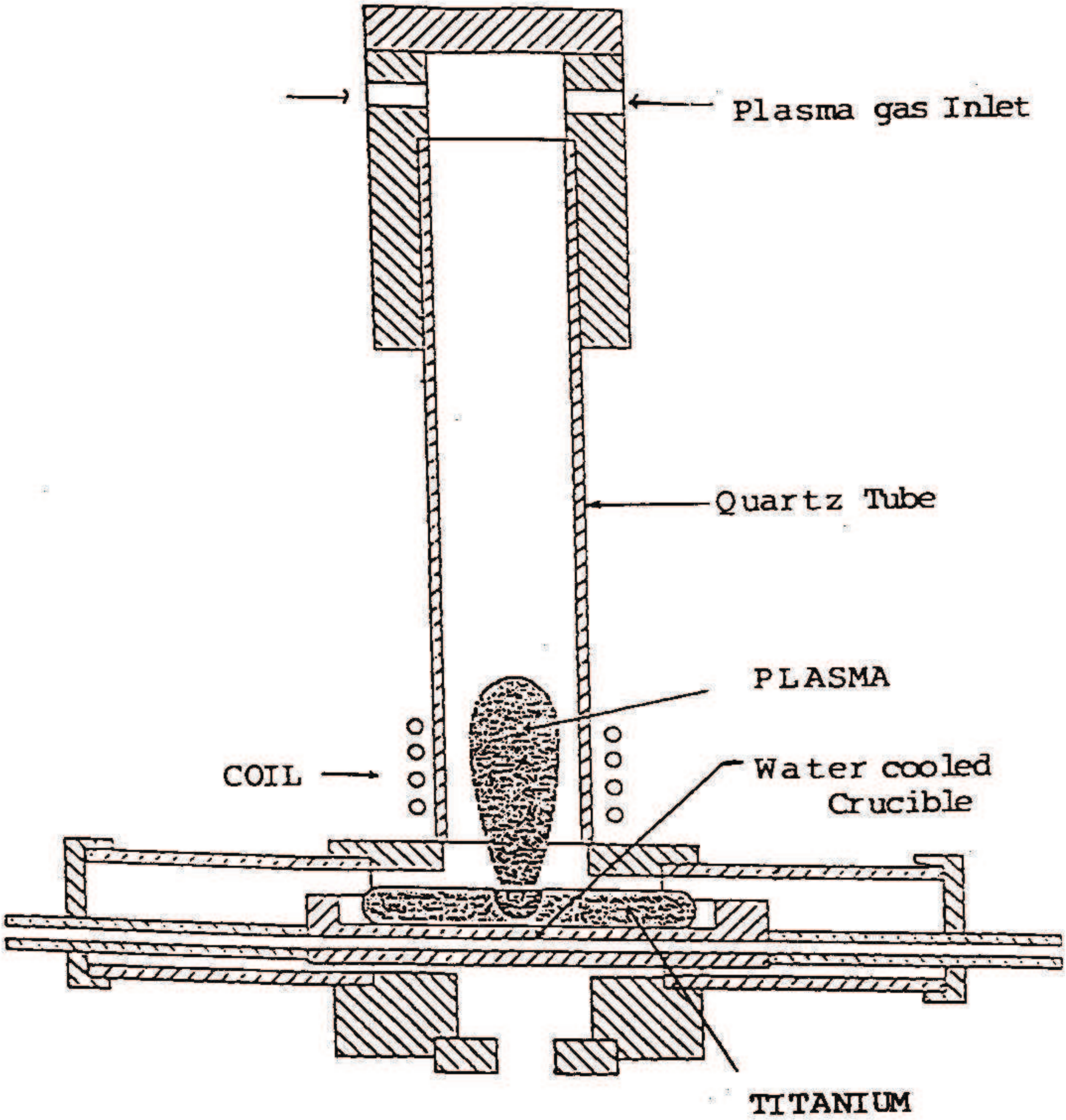


Fig. 5 - Set-up for titanium powders discontinuous melting

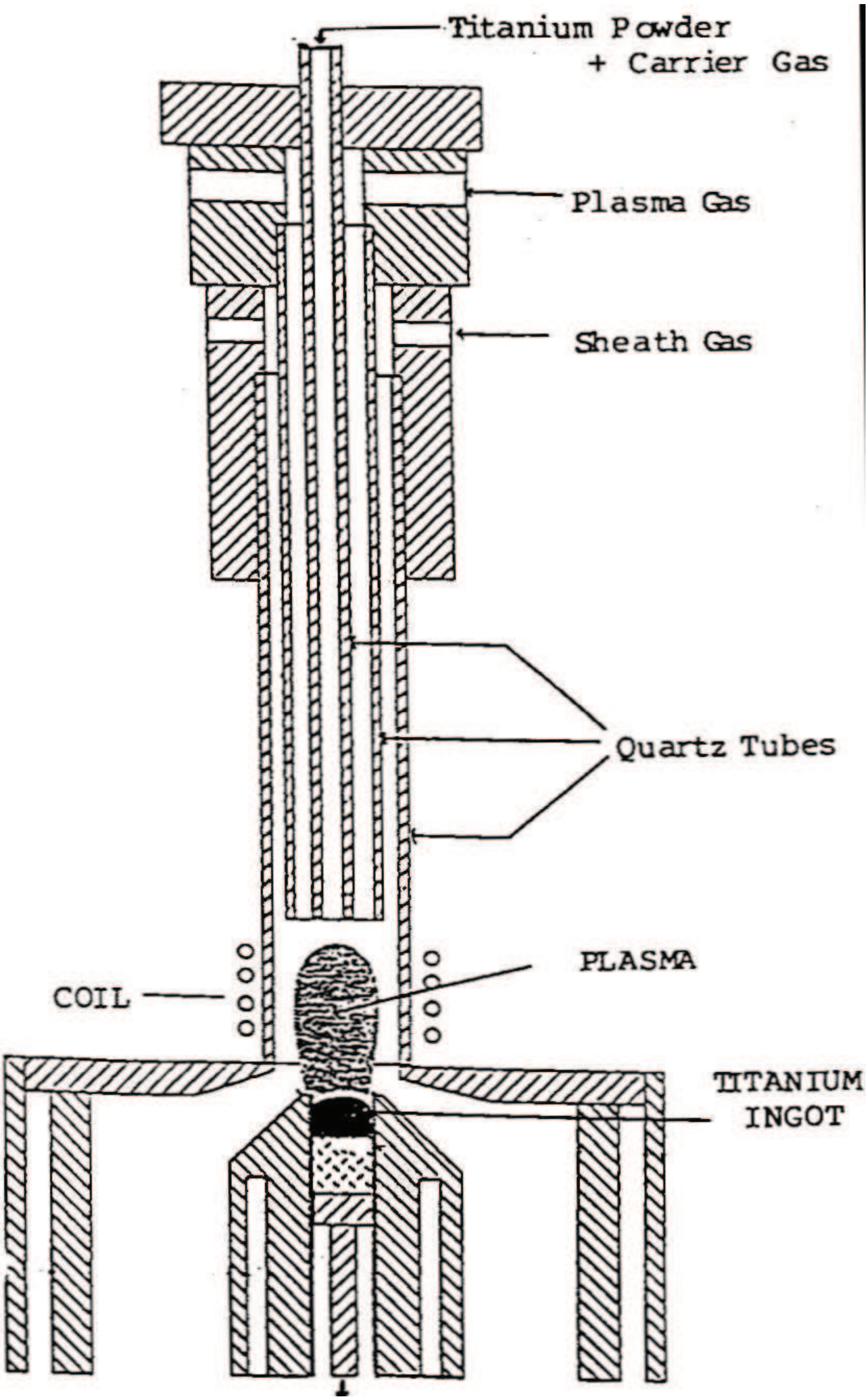


Fig. 6 - Set-up for titanium powders continuous melting

Discontinuous reactor - Operating conditions:

$P = 8$ kW - $Q_{Ar} = 30$ l/mn - $Q_{He} = 2.2$ l/mn

	Content (µg/g)	
Element	Starting Powder	Final Product
Cl	1122	Not detectable
Na	652	Not detectable
Fe	229	124
O	< 5000	1910
N	< 150	463
C	< 1500	110

Fig. 7 - Purification of a titanium powder melted by an argon-helium plasma

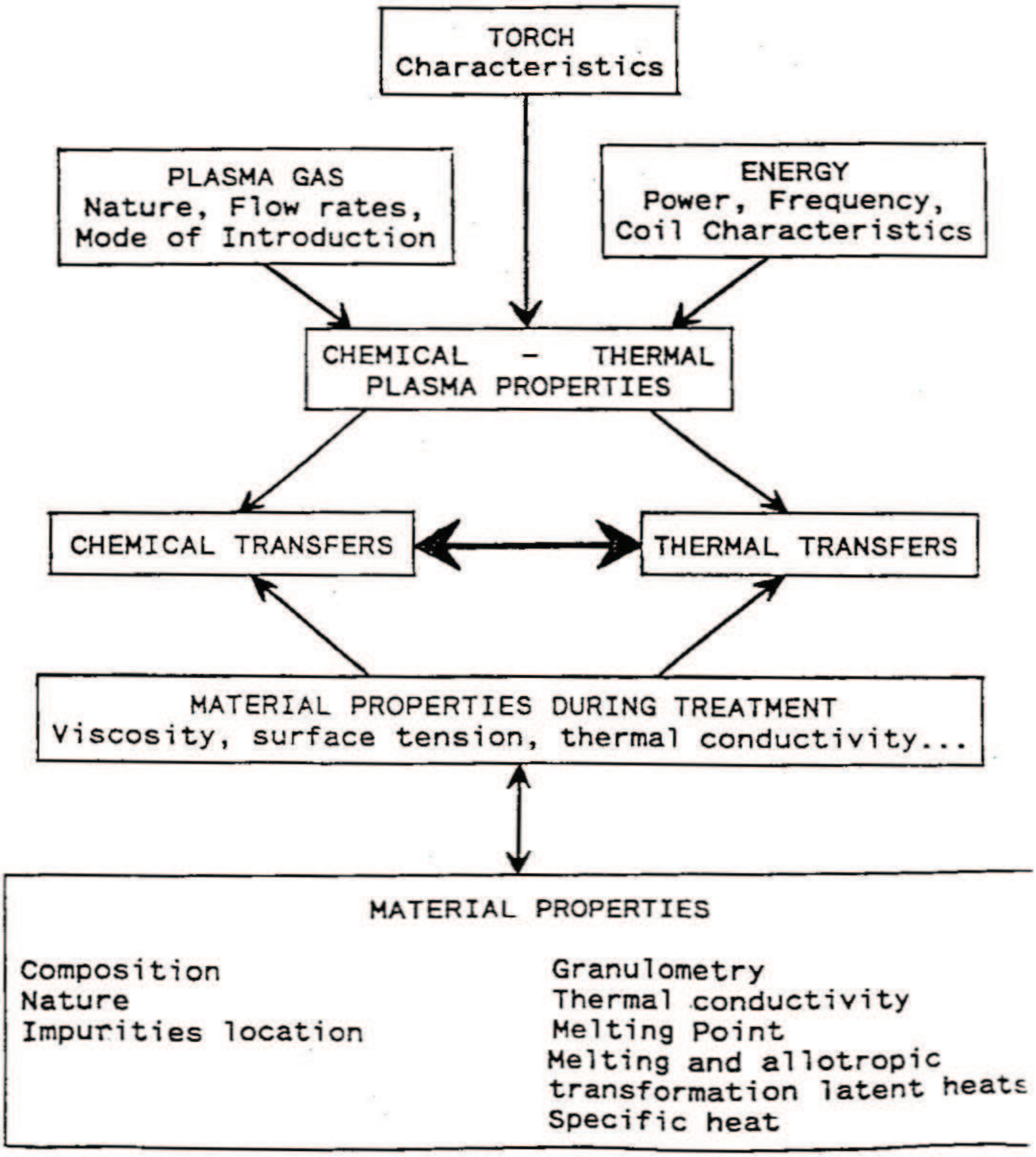


Fig. 8 - Key parameters for the plasma process

I. RAW MATERIAL PURITY LEVEL

	Contents in µg/g		
Material Element	Microsponge	Powder	Turnings
Cl	1971	689	<12
Cu	1617	78	17
Mn	391	6.0	14
Na	187	1008	7
Co	67	0.3	0.8
Cr	3100	31	89
Fe	30660	82	320

II. OPERATING CONDITIONS

Treatment of pellets composed of
Titanium powder and microsponge
P = 8 kW - Q_{Ar} = 30 l/mn - Q_{He} = 2.2 l/mn

Fig. 9 - Influence of raw material quality on the process efficiency

III. RESULTS

P : Eliminated % of Element X
pm : Microsponge % in pellets

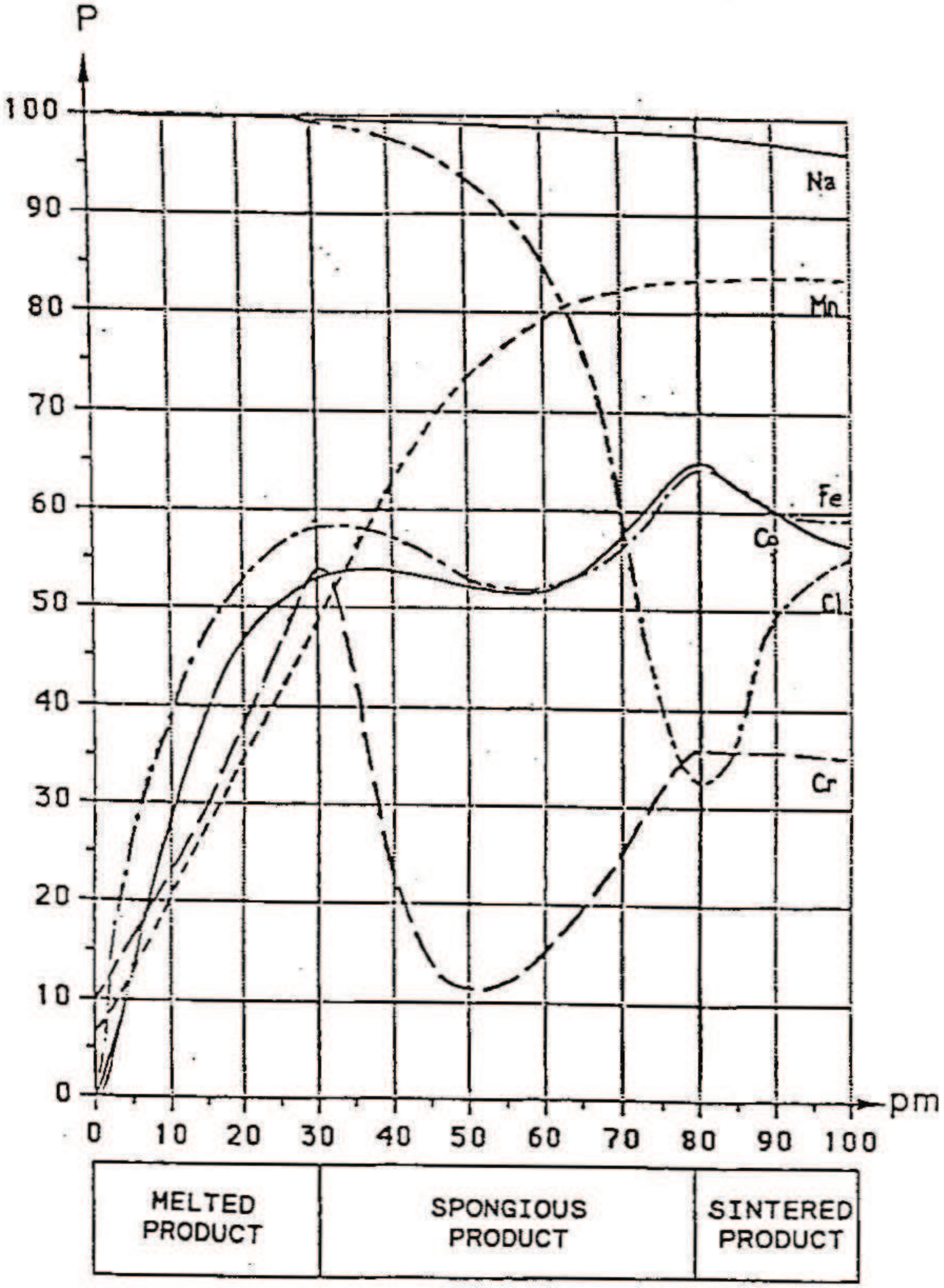
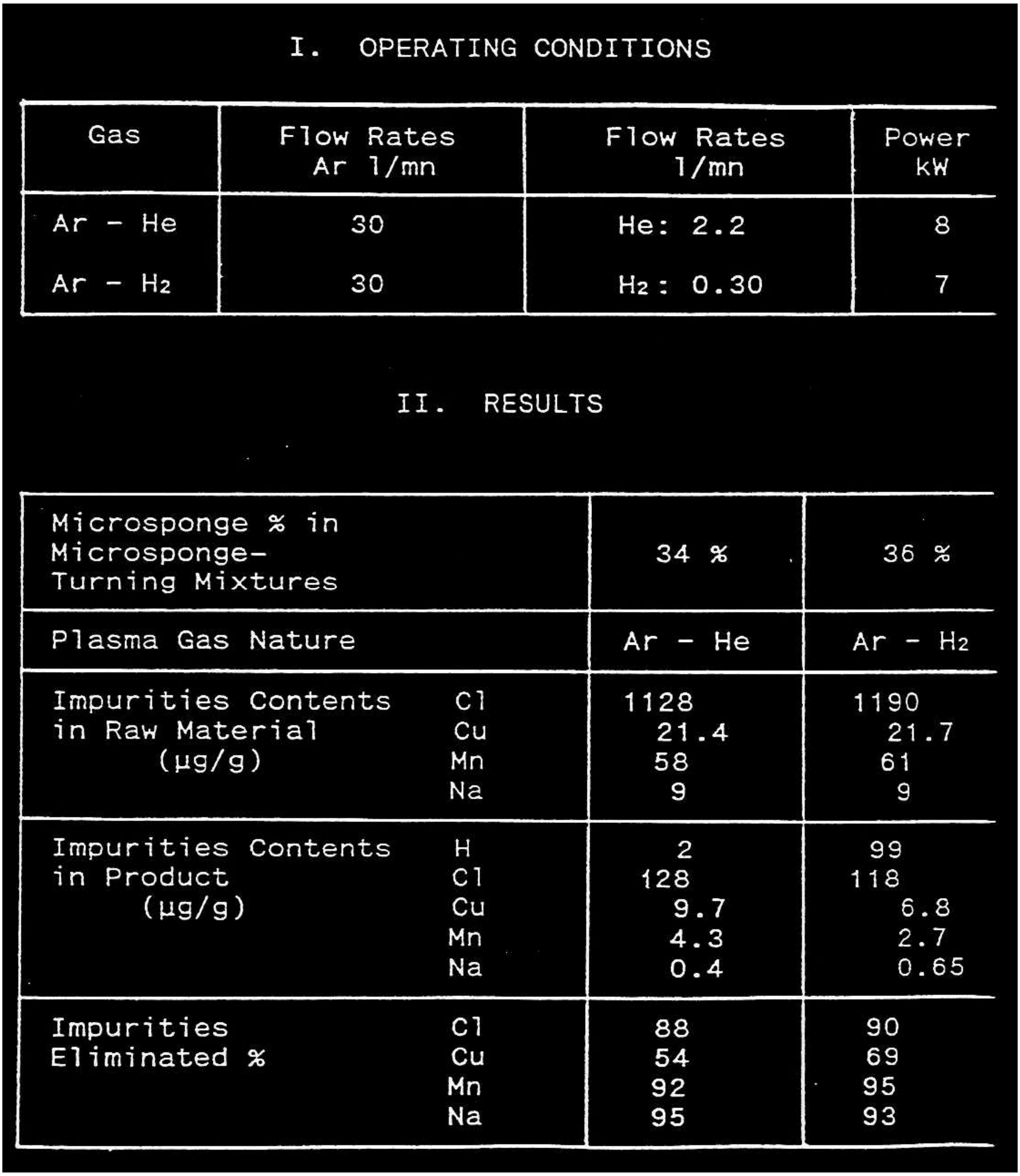


Fig. 10 - Eliminated % of impurities as a function of microsponge % in pellets



I. OPERATING CONDITIONS

Gas	Flow Rates Ar l/mn	Flow Rates l/mn	Power kW
Ar - He	30	He: 2.2	8
Ar - H_2	30	H_2: 0.30	7

II. RESULTS

Microsponge % in Microsponge-Turning Mixtures		34 %	36 %
Plasma Gas Nature		Ar - He	Ar - H_2
Impurities Contents in Raw Material (µg/g)	Cl	1128	1190
	Cu	21.4	21.7
	Mn	58	61
	Na	9	9
Impurities Contents in Product (µg/g)	H	2	99
	Cl	128	118
	Cu	9.7	6.8
	Mn	4.3	2.7
	Na	0.4	0.65
Impurities Eliminated %	Cl	88	90
	Cu	54	69
	Mn	92	95
	Na	95	93

Fig. 11 - Influence of gas plasma composition on titanium purification

OPERATING CONDITIONS:

P = 8 kW - Q_{Ar} = 30 l/mn - Q_{He} = 2.2 l/mn

	Contents in µg/g			
Element	Raw Material	Product		
		Without Flux	With 1% CaF_2	With 0.5% NaF
Cl	1074	49	136	133
Mn	121.5	82	66.6	59.5
Na	762	<0.03	0.53	1.64
Cr	952	830	541	711
Fe	9255	4750	2600	3620

Fig. 12 - Flux effect on titanium purification

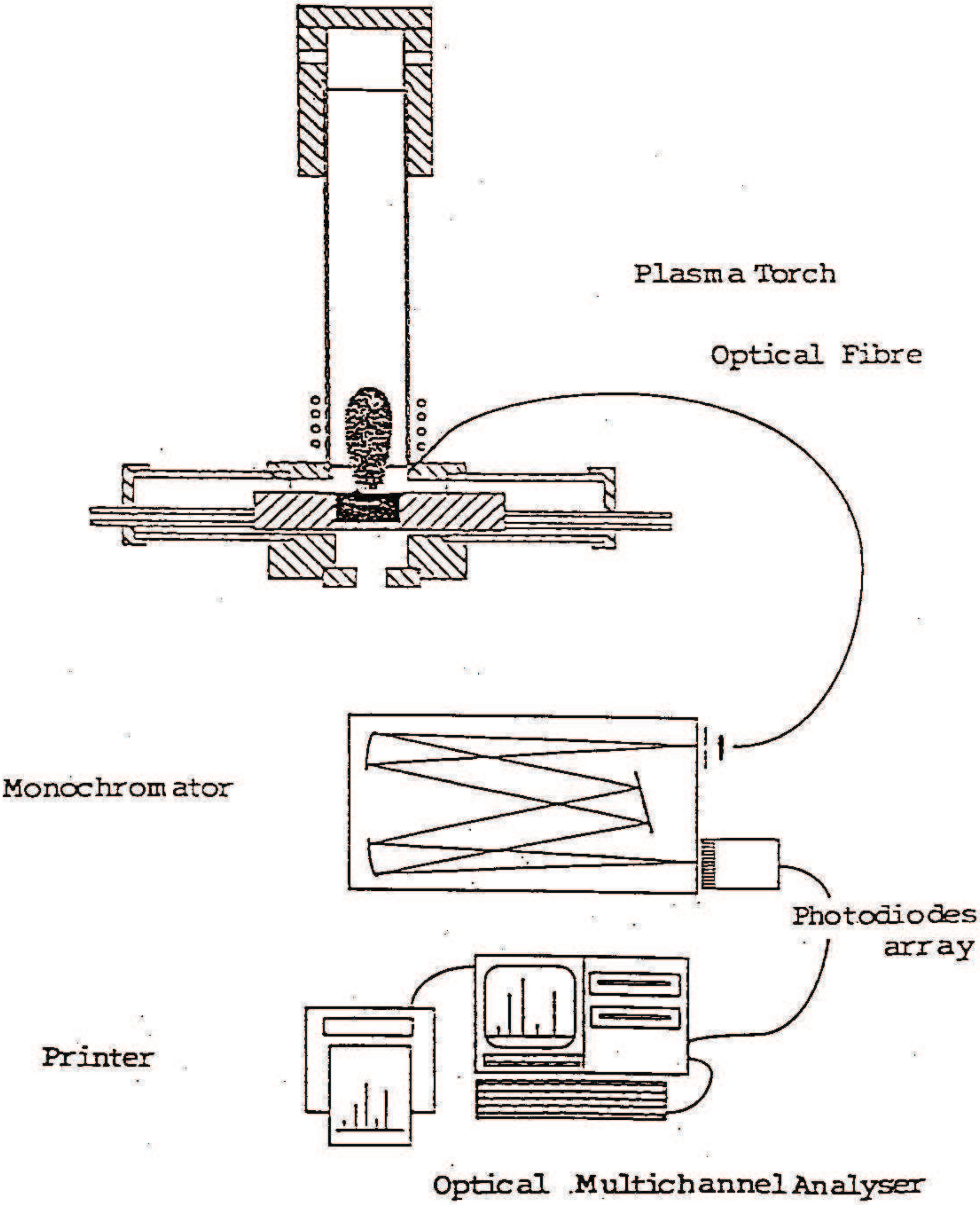


Fig. 13 - Experimental set-up for the purification follow-up

OPERATING CONDITIONS:

- Plasma : Q_{Ar} = 30 l/mn - Q_{He} = 2.2 l/mn
- Raw Material : Microsponge-Powder Mixtures (40% - 60%)
- Flux : LiF, NaF, KF, MgF_2

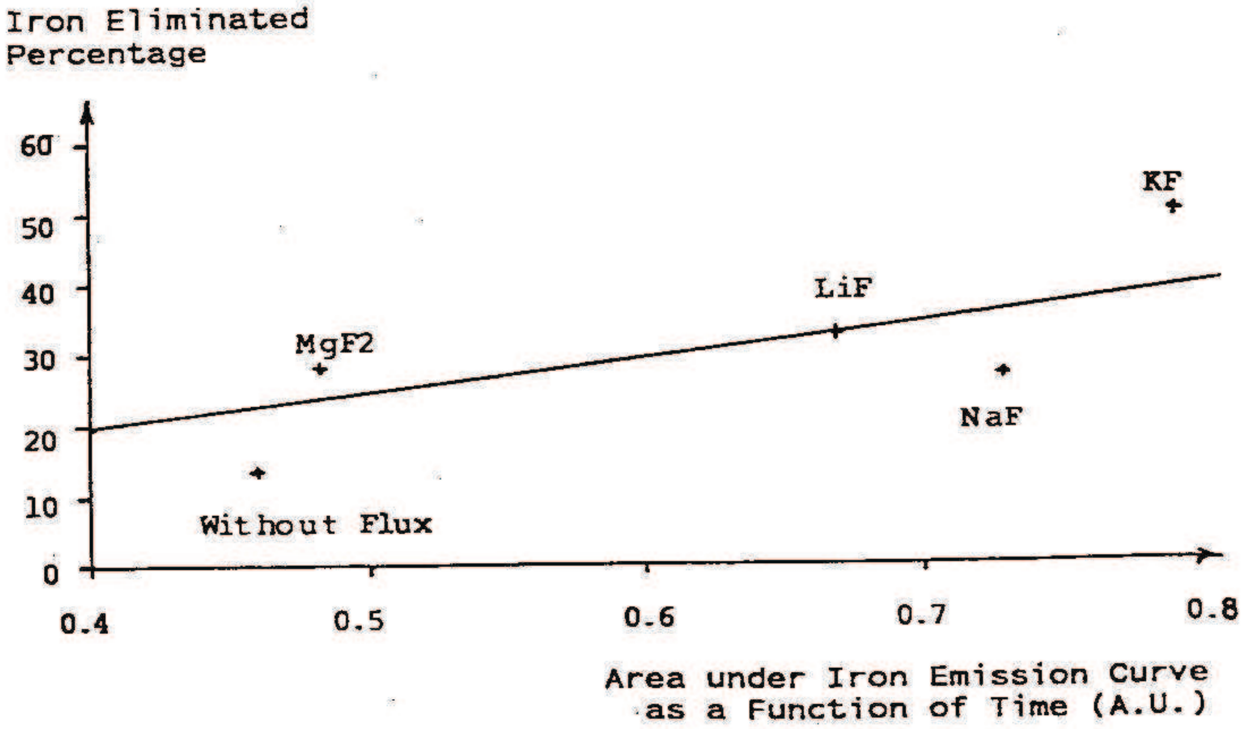


Fig. 14 - Titanium purification follow-up

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TITANIUM APPLICATIONS IN BATTERIES

Ladies and Gentlemen, I would like to set out the possible applications of titanium in electrochemical power sources. The aim of this survey is to give a comprehensive idea of the possible application of titanium as improver of electrode in batteries, both primary and secondary, that is storage and fuel cells. This survey is based on more than 300 patents since the 1970s. We will shortly see the use of titanium in lead acid storage battery grids, in this there are more than 15 patents, and some few examples of the use in other storage systems.

In lead acid storage batteries we can see why an attempt is made to substitute lead with titanium. There we can see the comparison table, mainly the mechanical properties and the weight. Of course this is more dedicated to some applications where cost is not the main thing to take into account. We can see here one patent and it was applied on a Fiat electric vehicle, on the lead acid battery, with positive grids in titanium and the negatives were in plastic, in polypropylene.

We have seen that the weight saving may be from 30 to 50% on grids and we gain on capacity from 15 to 20%. The advantage is that if the plate lead fails, titanium doesn't dissolve. There is another application with titanium alloys, titanium and 5% tantalum; this is good also for negative grids. We have seen the drawings of the composites, that is very interesting for creep resistance and we have seen the patent with titanium extruded lead wires and the titanium wires in grid casting.

We have seen also the bipolar electrodes by the Allied Corporation. We have done some research in Fiat also for electric vehicle batteries using titanium sheets for a zinc-bromine battery. The titanium sheets were with one side activated by the De Nora systems, with some ruthenium oxides. That battery was developed by Magneti Marelli on government funding in 1972. This zinc-bromine battery is now under development by Action, Toyota, Johnson Controls, Sanyo Laboratories.

A lithium-titanium sulphide secondary battery is under study at Jet Propulsion Lab. in Pasadena.

Last is a redox system using two different valences of titanium: Ti_4 plus electron is Ti_3 in some fuel cells. An interesting application for electrodes is being studied in France by the Agence Nationale pour la Valorisation de la Recherche, that took out an interesting patent on some titanium alloys with niobium, molybdenum, tantalum, zirconium. I have added some bibliographic indications for those who would like to go deeper into details and I am, through friend Ginatta, ready to answer single questions also by letter if you want.

Thank you very much for your attention and I hope this rapid survey will stimulate the research and development of this very interesting field.

Thank you!