# V MEETING SUL TITANIO

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GTT

GINATTA TORINO TITANIUM

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Marco V. Ginatta
Ginatta Torino Titanium
INTRODUZIONE AL CONVEGNO

Signore e Signori Buon Giorno. Benvenuti a questo quinto incontro fra l'industria del titanio e gli utilizzatori di tutti i settori industriali.

Anche quest'anno la GTT ha il piacere di organizzare questo evento e la soddisfazione di vedere crescere la partecipazione degli operatori a questo nostro appuntamento annuale.

lo sono Marco Ginatta e, ringraziando tutti i convenuti, apriamo i lavori di questa giornata che dal programma si annuncia molto intensa.

Come sapete, le finalità e gli obiettivi di questo incontro sono di contribuire alla diffusione delle informazioni tecniche e commerciali sul Ti e leghe e di dare opportunità di conoscersi fra operatori di settori industriali non ancora serviti dall'industria del Ti e i produttori di titanio.

La reciproca conoscenza delle caratteristiche delle attività dei vari settori industriali permette di fare emergere le opportunità di vantaggiose applicazioni del Ti.

Passando in rassegna gli ultimi 12 mesi dallo scorso meeting del 1988, vediamo quali sono stati gli avvenimenti principali nell'industria del Ti.

Il più importante è rappresentato dall'ottimo andamento del mercato che continua sui massimi livelli dallo scorso anno e si prevede continuerà fino al 1993 per quanto riguarda il settore degli aerei commerciali; mentre il mercato delle applicazioni industriali continua la sua rapida crescita e si prevede diventerà presto il mercato principale del Ti.
L'unico freno che ha rallentato la crescita è stata la capacità produttiva installata nel mondo che è attualmente completamente utilizzata.

Ma abbiamo, a questo proposito, un' ottima notizia per quanto riguarda l'Italia.
Infatti è iniziata la costruzione dell'impianto di Terni della società Titania del gruppo ILVA e questa mattina avremo il piacere di sentire maggiori dettagli dal Rag. Timpani, Direttore Generale della Titania e dall'Ing. Proface, Direttore Tecnico Italimpianti del progetto, che parleranno fra breve.

Nuovi impianti:
Bob Wilde presenterà il nuovo impianto di arricchimento minerale destinato ad alimentare nuovi impianti per produrre Titanio.

Riguardo agli Stati Uniti, presso la Società RMI è entrato in funzione il primo reparto dell'Impianto elettrolitico con produzione di Ti di alta qualità.

La qualità del titanio è stata l'argomento dell'anno per gli utilizzi aeronautici, i costruttori di motori e strutture desiderano continuare la storia di eccellente affidabilità delle leghe Ti degli ultimi 40 anni.

Sull'argomento costo si è progredito molto il lavoro di convergenza fra i produttori di Ti dedicati alla riduzione del valore assoluto prezzo al kg e fra gli utilizzatori dedicati alla realizzazione dell'efficienza del costo nelle loro specifiche applicazioni.

La più recente occasione di verifica dei risultati del lavoro di sviluppo del mercato si è visto al Salone Nautico di Genova, recentemente tenuto, in cui le caratteristiche del Ti per usi marini sono state utilizzate in molte applicazioni.

Delle nuove applicazioni in tutti i settori dell'industria sentiremo parlare diversi oratori nel corso di questa giornata.

Vedremo come il Titanio si presenta alla soglia degli anni '90.

Infatti per il decennio che inizierà fra poche settimane il Ti ha tutte le condizioni per riuscire a coprire il suo ruolo fra i materiali metallici a servizio dell'uomo.

La storia dell'alluminio prima e quella dell'acciaio inossidabile poi, illuminano la strada dello sviluppo del Ti. Noi riteniamo che il Ti seguirà gli stessi stadi di sviluppo.

Quest'anno 1989 è il centenario della nascita del Dr. Kroll che cade proprio in questi giorni.

Noi abbiamo pensato di sottolineare questo anniversario con una testimonianza della nostra riconoscenza al grande scienziato - industriale con gratitudine per tutto ciò che ha fatto per lo sviluppo dell'industria del Ti.

A tutti gli oratori diamo una targa ricordo di questa occasione.

Abbiamo l'onore di avere qui oggi con noi il Dr. Moore della Colorado School of Mines, che è il Direttore dell'Istituto Kroll, al quale abbiamo il piacere di consegnare questa targa a ricordo del Dr. Kroll e del nostro meeting di quest'anno.

# W. J. KROLL: "A METALLURGIST OF THE UNUSUAL: THE AMPHIBIOUS AND RECALCITRANT LONE WOLF RESEARCHER"

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## Introduction

William Justin Kroll was born in Esch/Alzette, Luxembourg in 1889. Although W. J. Kroll's name is most often connected with extractive metallurgy -- especially the production of ductile titanium and zirconium, his research interests and achievements span a wide area of process metallurgy, including age hardening alloys, improving the ductility and strength of both non-ferrous and ferrous alloys, grain refining, and purification of metals. Dr. Kroll's research achievements in the extraction of titanium and zirconium are well known. However, I would like to concentrate a little more in this presentation on demonstrating the other significant research achievements of Dr. Kroll -- achievements which indicate that he was indeed an extraordinary process metallurgist.

Professor F. D. Richardson of the Royal School of Mines, London, in his address in 1974, celebrating the centenary of the Colorado School of Mines and the dedication of the W. J. Kroll Institute for Extractive Metallurgy, stated that, "William Kroll's career is notable for the merit and originality of his work and for his great persistence". These three qualities best describe W. J. Kroll's approach to metallurgical research.

In his paper published in the Journal of the Franklin Institute in 1955, Dr. Kroll stated that, "in any invention of importance one is first to examine the educational background of the inventor and his mental preparation and development". William Kroll's educational background in metallurgy started as a small child. His father was a blast furnace manager and his grandfather an operator of an iron ore mine. He wrote of an early recollection: "a far-away picture still remains in my mind, when, as a child, in the darkness of a cold morning I was taken out of bed to light a new blast furnace with a bunch of cotton, impregnated with burning kerosene and fastened to the top of a long pole".

W. J. Kroll was a highly independent researcher who focused on industrial problems in a creative and innovative way. He was indeed a visionary in the process metallurgy field. He believed in the sound application of physical science principles and had a healthy regard for safety while conducting his experiments.

William J. Kroll was awarded the following honors for his outstanding work:

Student Medal - Technischen Hochschule
Perkin Medal - Society of Chemical Industry
Francis J. Clamer Medal - Franklin Institute
James Douglas Medal - American Institution of Mechanical Engineers
Heyn Medal - Deutsche Gesellschaft Fur Metallkunde
Albert J. Sauveur Award - American Society for Metals
Gold Medal - American Society for Metals
Castner Medal - Society of Chemical Industry (Great Britain)

Acheson Medal - American Electrochemical Society
Platinium Medal - Institute of Metals, London
Gold Medal - Institute of Mining and Metallurgy, London

Honorary Degrees from:

University of Brussels
University of Grenoble
Oregon State University
University of Missouri

Getting to Know Kroll Through His Quotations

In conducting the background research for this presentation, I feel the main resource from which I have become more acquainted with W. J. Kroll is from quotations that he has made in some of his early papers. One such quotation taken from his presentation on receiving the Perkin Medal Award in 1943 indicates how he felt about his profession. He writes, "it must have been quite difficult for the Perkin Medal Committee to define my true profession since metallurgists are of a complex nature and they might split, like some atoms, in various fission products. These splits may be physical, extractive, pyro, hydro, electro, thermodynamic, ferrous and non-ferrous, besides the many varieties of cross breeds with technologists. Having been wandering around in most of these groups, peeping in their melting pots, sometimes brazingly suggesting improvements in their methods while knowing very little about their art, I became in the course of the years somewhat amphibious and I am often perplexed when asked what my profession is. My answer may be, that I always use 'The metallurgist of the unusual'".

In reference to the above quotation, Kroll was mainly interested in the unusual or rarer metals. He goes on further to state that, "good metallurgists are not born. They are made with the ample money of the companies which hire them, and since they usually make their mistakes on a grand scale, they are the nightmares of business management".

A further quotation which indicates Dr. Kroll's approach to research and his belief in the independent researcher is also recorded here: "the fight of the individual with an independent mind against the collectivity in which he lives is as old as humanity, they will never cease to exist".

During the course of this presentation, I will use further quotations which indicate Kroll's humor and dedication to his work.

## Kroll the Itinerant

Dr. W. J. Kroll was also somewhat of an itinerant in that he was born in Luxembourg in 1889, and studied at University at Charlottenburg in Germany from 1910 to 1917. He was employed by Metallgesellschaft in Frankfurt/Main from 1917 to 1919, moved to Vienna in 1919, and then Hungary between 1920 and 1921. He moved to Baden-Baden in 1922 and returned to Luxembourg in 1923. In 1940 he emmigrated to the U.S.A. to escape Hitler's invasion of Luxembourg. He remained in the U.S.A. until he retired to live near his brother in Brussels. Dr. W. J. Kroll died in 1973.

## W. J. Kroll's Accomplishments

In order to appreciate the wide range of achievements of William Justin Kroll, it is interesting to chronologically list his investigations, developments, research findings and discoveries. Like all good researchers he used the knowledge gained through a previous investigation to implement and support the current and future research programs. This trend can be clearly seen in the following outline of Dr. Kroll's achievements.

The Early Years. From 1910 to 1917 Dr. Kroll studied at the Technischen Hochschule in Charlottenburg, Germany where he studied iron metallurgy and worked as an assistant to Professor W. Mathesius. He completed his doctoral thesis under the supervision of K. A. Hofman on the production of pure boron. He states that, "this influenced my future life deeply, for I never strayed far from the chosen field of preparative chemistry".

In 1917 he was employed by Metallgesellschaft in Frankfurt/Main and was sent to the lead refinery at Call/Eifel. There he developed a process for producing calcium-barium-lead bearing alloys by injecting sodium into a bath of lead containing barium and calcium chlorides. Figure 1 shows the schematic representation of his sodium injector from producing the calcium-lead alloy. He also worked on the development of a process to debismuthize lead and techniques to remove antimony and arsenic from tin alloys using aluminum.

Kroll's research work was not without certain disasters. One such incident was a huge fire initiated by the injection of sodium into the lead bath. He later commented that the skills which he developed from this incident would have fitted him well as a fire fighter in the London Blitz of the Second World War.

In 1919 he moved to Vienna to study a process from removing tin, silver, and gold from antimony-copper-tin residues produced from smelting church bells (a valuable materials resource in war time). Once he had developed the technology from this operation, he was recruited by the Hungarian government to build, with the help of personnel from the large Manfred Weiss, Csepel works, a plant from processing such church bell residues. The plant he constructed consisted of one shaft furnace, two converters, one reverberatory furnace, and an existing tin copper electrolysis plant.

Dr. Kroll recalls the first night of operation in which he was called out in the middle of the night on account of the bag house being destroyed by sulfuric acid present in the fumes. His response to this disaster indicates the man's ingenuity. With no immediate help available, he quickly solved the problem by sending someone to the local brewery to obtain cylinders of liquid ammonia to neutralize the bags by implementing a procedure of spraying the bags every few hours. Kroll's instructions to the bag house attendant was, "to apply to each chamber, after shutting it down and shaking the bags, enough ammonia until it started smelling".
The humor of W. J. Kroll is also noted in a quotation describing his observations of an important ceremony at the large Csepel works, he

states, "I had a great time at this plant, located on the island of Csepel on the Danube. This is because I had the opportunity of watching the work going on in this huge mill, which occupied at one time 20,000 workers. For instance, there was that job of casting new church bells for the next war. A German specialist was called upon and he started making molds and cores from manure, clay, and stale beer, a secret which had passed on from generation to generation in his family. These molds were then carefully dried after having been decorated with angels and pious inscriptions and works, exactly as described in 'Schillers Glocke'. My German had chosen a reverberatory furnace in which to melt these metals and to make his bronze, and he intended to cast a good dozen of bells while in operation. But he made his calculations without considering the oxidizing properties of his reverberatory furnace, which, as shown by the events, burned up the tin, forming a difficult fusible slag. The day of the great tapping all top figures of the city of Budapest had appeared, including the Admiral Horty and the Archbishop Prochaska. They were neatly dispersed around the furnace, in comfortable plush seats from which they could watch the pouring of the bells, which they had dedicated and which carried their name on a board wherever the molds laid buried on the ground. Meanwhile, my German was busy trying to get his metal out of the furnace, while one inspiring speech after the other was released until even the low quality spare ones were exhausted. Then came the moment when oxygen had to be put to work to save the situation to open the tap hole by chemistry. This operation was finally a success and the metal was gurgling happily out and filling the runners and molds, the latter, however, only partly, because too much metal had been burned up in the furnace. The faces of those, who had dedicated a bell and who had gotten only half of their deal, turned sour, and since nothing can be done with half a bell, they went home quite dissatisfied. But with much money spent in experiments, the company finally became experts in casting bells."

In 1922 Dr. Kroll left Hungary to set up a research laboratory in a small foundry in Baden-Baden. Here he developed a light weight, low expansion piston alloy which had good wear resistance and creep strength. This was a hypereutectic 23% silicon aluminum alloy with small additions of copper. He also developed a high creep strength magnesium alloy which contained mischmetall which was used in superchargers of aviation motors in World War II. This alloy was subsequently copied by U.S. metallurgists after examining planes that had been shot down.

<u>The Productive Years in Luxembourg.</u> In 1923 Kroll decided to return home to Luxembourg and to establish his own research laboratory in a large house (Figure 2) with one unskilled laborer, one mechanic, and one secretary who also performed some metallographic and spectrographic work. Of this venture, he is quoted as saying, "at that time such a project of a single man, working with his bare hands with only the wits of his mind had to be considered by a normal metallurgist as a kind of lunacy". However, this was a very productive period for Dr. Kroll. During this time he developed the process for debismuthizing of lead which was later commercialized by the American Smelting and Refining Company. He also developed a process for vacuum dezincing of lead produced from the Parkes

desilverization process. This process is outlined in Figures 3 and 4 and was later commercialized by W. T. Isbel of St. Joseph Lead Company.

Kroll also worked on age hardening of aluminum, in particular investigating substitutes from silicon, magnesium, and copper and developed a silver-aluminum alloy; a lithium-bearing aluminum-zinc alloy and magnesium-germanium-aluminum alloys. He also studied the germanium-aluminum phase diagram and the replacement of silicon with germanium crystals in radar detectors.

While working on fused salt electrolysis of beryllium, Dr. Kroll became beryllium poisoned in 1927 but stilI managed to develope the process for the reduction of anhydrous beryllium fluoride with magnesium.

It was at this time that Kroll became interested in the application of vacuum metallurgy in the extraction and purification of metals. Since he was not allowed into the local Heraeus plant he had to learn vacuum technology and methods by himself. He subsequently developed a process for the vacuum reduction of BaO with aluminum to produce barium metal, and the production of high quality calcium by vacuum sublimation of electrolytic grade calcium cast under an argon atmosphere. This period of work gave him the initial background for his subsequent development of titanium and zirconium extraction metallurgy.

The high purity calcium he produced in this period, he used as a reductant in a bomb reactor for the production of ductile chromium, vanadium, titanium, zirconium, uranium, and thallium. He also worked on the vacuum purification of silicon, copper, iron, chromium, beryllium, and alloys of copper, tin, and lead during this period.

In 1930 Dr. Kroll became interested in the reduction of titanium and initially investigated the reduction of $TiCl_4$ with sodium in a flash reaction process, but stated that this process would never become commercial on account of the high pressures created by such a reaction. He then looked at the reduction of $Ti0_2$ and $ZrO_2$ with pure calcium under an argon atmosphere in 1935.

In 1937 he started his first experiments on the pressureless reduction of $TiCl_4$ with calcium under an argon atmosphere and produced 250 grams (88% yield) of cold ductile titanium. On July 30, 1937 Dr. Kroll first experimented with the use of magnesium as a reductant for $TiCl_4$, eventually producing titanium of 180 Brinel hardness using a large stainless steel reactor. On July 13, 1938 he produced zirconium from a similar reaction involving zirconium chloride reduced with magnesium using the same equipment, and vacuum separation of the sponge zirconium from the surplus chloride.

In the Autumn of 1938 W. J. Kroll visited the U.S.A. in an effort to sell his titanium reduction process taking his titanium samples with him (Figure 5). Unfortunately, he found no interest and "left the United States in a sad state of mind, not having been able to interest anybody in my ideas".

While working on his main projects, Kroll was frequently interrupted to examine other process metallurgy areas. A sample of these include: iron-beryllium age hardening alloys; partial substitution of nickel for beryllium for providing increased hardness and grain refining; substitution of titanium or aluminum for beryllium in nickel-steels to produce age hardening; the use of chromium to provide hardenable stainless steels; and the precipitation hardening of Mg + C in nickel alloys, -- this was later taken up by the International Nickel Company in 1932.

Dr. Kroll also spent a large amount of his time investigating the purification of metals. In particular the vacuum distillation of chromium, manganese, beryllium, iron, tin, zinc, lead, and their alloys.

The USA Years. On February 10, 1940 William Justin Kroll emmigrated to the U.S. from Luxembourg, two months ahead of Hitler's invasion of his country. He stated, "I have abandoned all of my belongings, the whole equipment of my laboratory, and the big estate. Luck was with me since I got it back again in 1947, almost intact".

From 1940-1945 Dr. Kroll worked in the Union Carbide Research Laboratories at Niagara Falls as a consultant. In his own words, "this was a fertile time". He investigated diffusion electrolysis with soluble and insoluble anodes to produce iron, chromium, and magnesium powders; the production of anhydrous chlorides of magnesium and zirconium; the use of chlorides reacted with powdered solid alloys to extract unwanted constituents, such as copper from Monel metal and iron from iron-nickel; the separation of tantalum and niobium by hydrogen reduction of their oxides; the reduction of uranium oxide with calcium; the silicothermic reduction of magnesium; the production of electrolytic calcium; the production of sodium from NaCl using silicon and lime in vacuum.

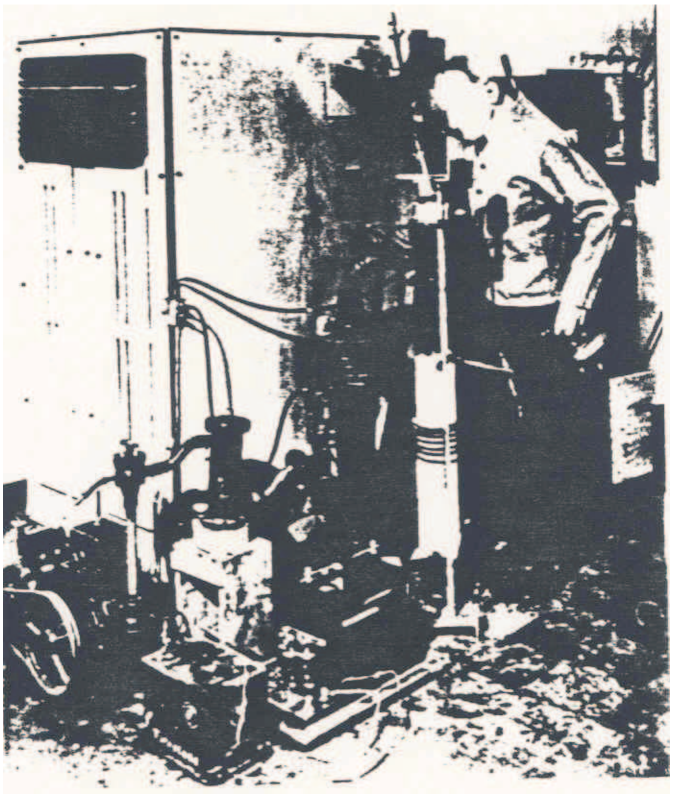
In December 1945 he joined the U.S. Bureau of Mines Albany Research Laboratory and took over the zirconium research program having spent the previous 18 months as a consultant on this project. In August 1946 he was able to roll the first strip of zirconium (Figure 6) ably assisted by Dr. A. W. Schlechten, who later became Head of the Department of Metallurgical and Materials Engineering, the Colorado School of Mines and the founding Director of the Kroll Institute of Extractive Metallurgy.

It was indeed fortunate that Dr. Kroll's ingenuity and research expertise in process metallurgy had been utilized in order to make zirconium available at the time when it was needed for the first atomic submarine reactor.

In 1950 Dr. Kroll resigned from the U.S. Bureau of Mines to work as a private consultant from his home in Corvallis, Oregon. During this period, Dr. Kroll's titanium patent was subjected to a long period of litigation before he was awarded all the royalties from titanium produced from his process. This legal process had a detrimental effect on Kroll's health. In 1965 he moved to a suburb of Brussels to be near his brother, Theodore, but continued his close association and friendship with Dr. A. W. Schlechten at the Colorado School of Mines.

## A Final Comment

Dr. Kroll died in 1973. All through his professional lite he was insistent on the need for independent researchers to be allowed to conduct their research. In this respect he commented, "we have to offer the recalcitrant lone wolf researcher a kind of an asylum, since this useful species is lately menaced by extinction". It is, in fact, fortunate that this particular lone wolf researcher had the commitment to pursue his dreams and, in so doing, the world of metals and metals production is immensely the richer. Dr. Kroll's final sentence in his presentation on receiving the Perkin Medal from the Society of Chemical Industry in 1943 actually summarizes his great satisfaction in conducting research of the unusual, "I am happy that a gracious fate has allowed me to carry, for a while, the flag of rare metals research, around which many young men have now gathered to carry on, where I have left off".



Dr. W. J. Kroll working in his laboratory.

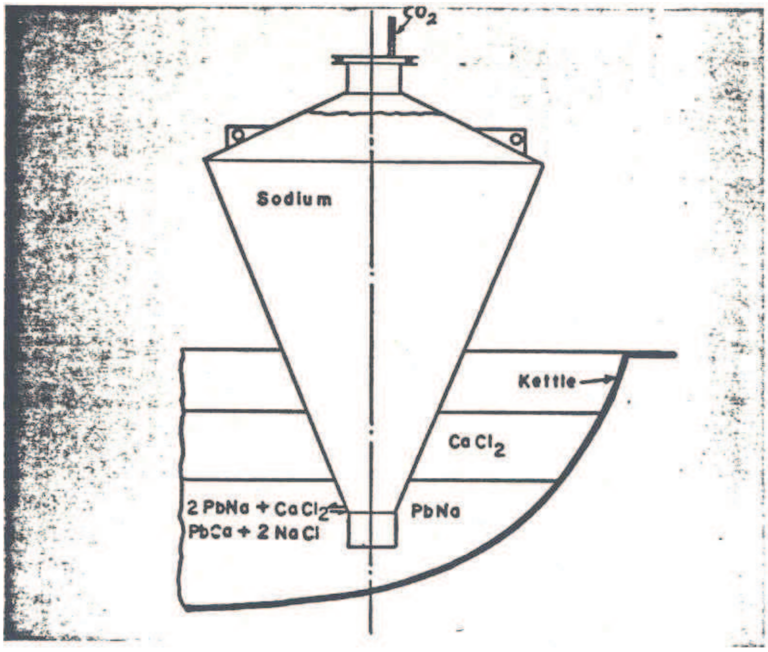


Figure 1 - Schematic representation of sodium injector for producing Ca-Pb.

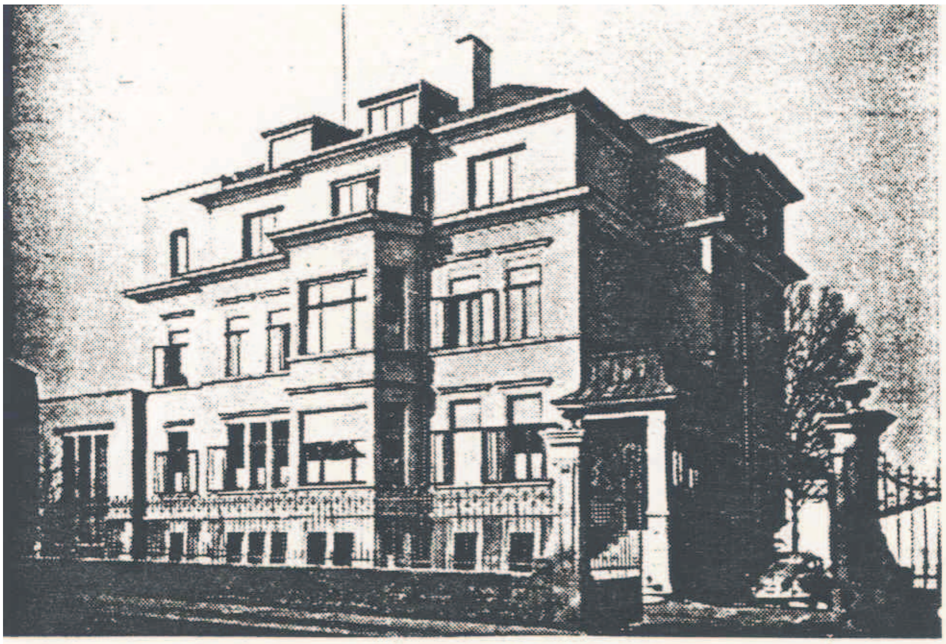


Figure 2 - Kroll's laboratory in Luxembourg.

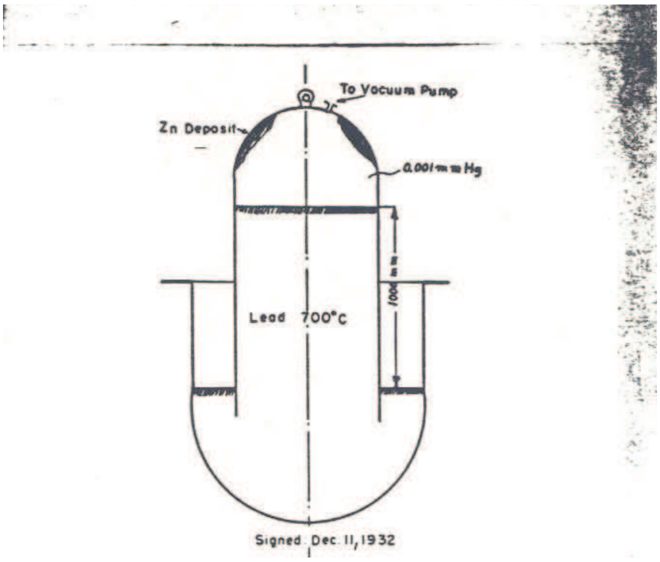


Figure 3 - Vacuum dezincing of Parkes lead (submerged bell jar).

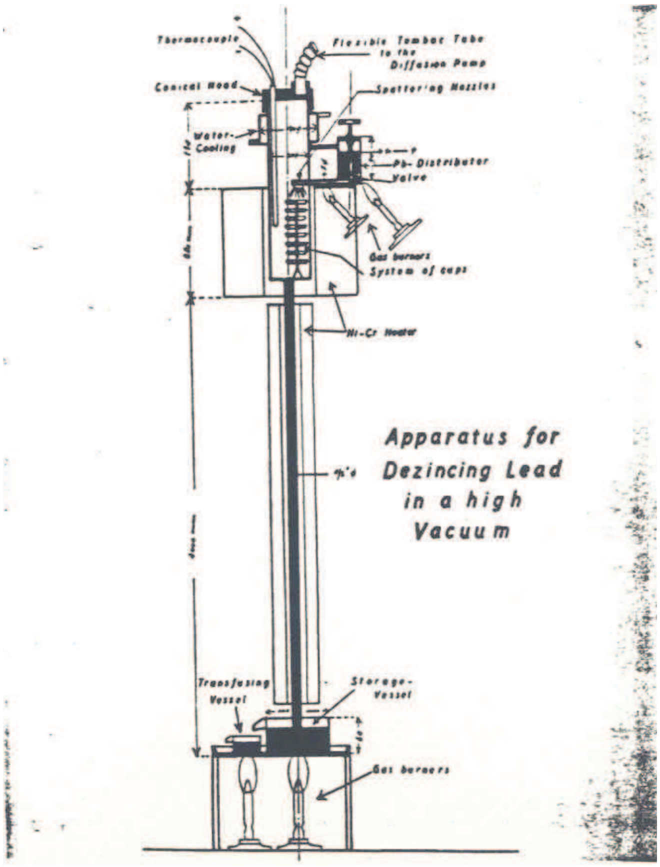


Figure 4 - Vacuum dezincing of Parkes lead (circulation and lead spray).

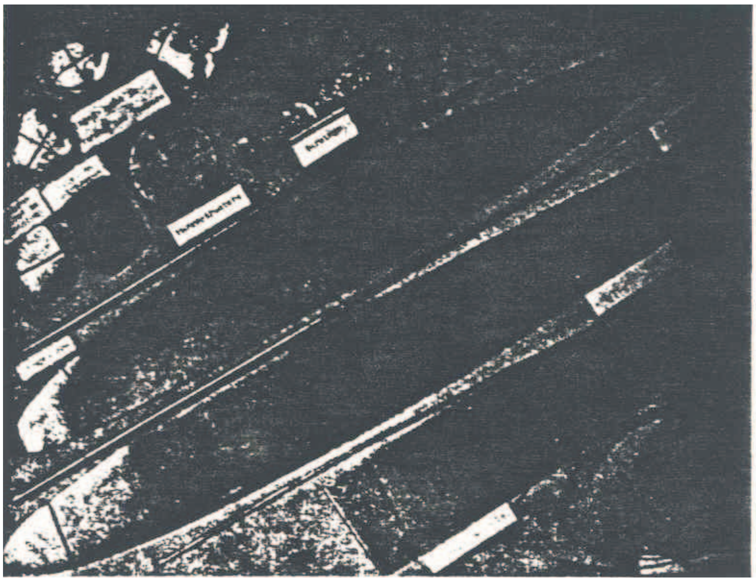


Figure 5 - Kroll's titanium samples produced in 1937.

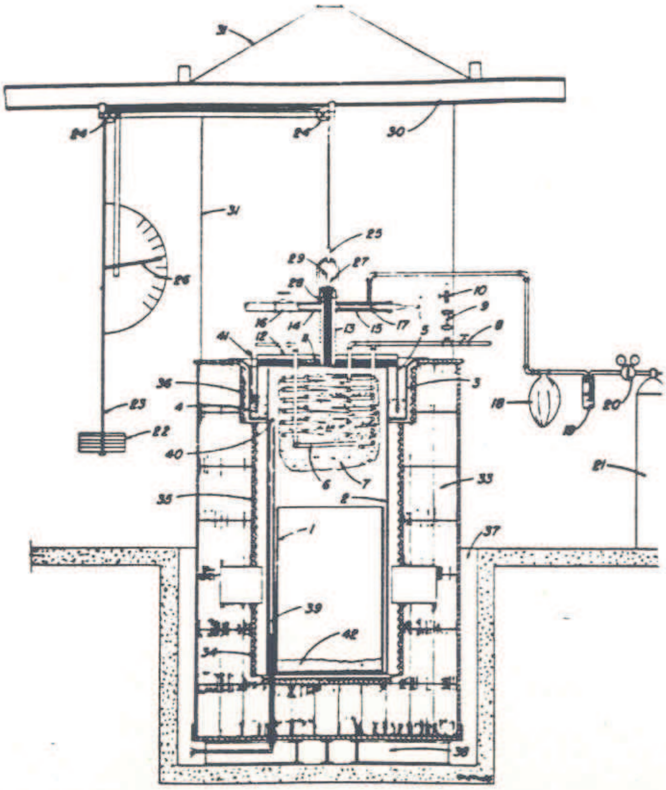


Figure 6 - Commercial equipment for zirconium extraction (USBM).

# V° MEETING INTERNAZIONALE
# SUL TITANIO

Torino, 9 Novembre 1989

GINO SESTO TIMPANI
TITANIA S.p.A.

## IMPIANTO DI PRODUZIONE
## TITANIO IN ITALIA

# MEMORIA PER IL V MEETING SUL TITANIO

## TORINO - 9 NOVEMBRE 1989

### Impianto di produzione titanio in Italia

L'ILVA che, come è noto, è subentrata alla FINSIDER nel piano di ristrutturazione e rilancio dell'industria siderurgica nazionale, ha sempre curato la produzione e lo sviluppo degli acciai speciali accanto a quelli tradizionali di massa.

TITANIA, che è la Società creata dall'ILVA per produrre titanio, rappresenta una "naturale" evoluzione di questa politica perché i prodotti in titanio e nelle sue leghe sono già oggi fungibili ad alcuni tipi di acciai, quali inossidabili e leghe speciali.

A base della decisione di intraprendere la produzione del titanio stanno infatti studi di mercato che dimostrano come il titanio in lega abbia vinto la concorrenza nelle applicazioni aeronautiche, e faccio specifico riferimento ai dati divulgati un anno fa in questa medesima circostanza, mentre ampie possibilità di applicazione si stanno aprendo anche per il titanio puro commerciale.

Cito alcuni esempi di questo tipo di applicazioni industriali :

- scambiatori di calore per centrali elettriche
- impianti di desalinizzazione e potabilizzazione
- costruzioni navali
- impianti protezione catodica di acciai nel cemento
- impianti chimici
- piattaforme petrolifere

ed altre non meno importanti che per ragioni di tempo non elenco.

La tipologia degli utilizzi lascia prevedere la possibilità di grossi spazi di mercato ben compatibili con la disponibilità di titanio in natura ma con accessibilità limitata dall'alto costo attuale del prodotto che di conseguenza si è soprattutto sviluppato nel settore aeronautico.

L'ILVA, già da alcuni anni presente nel mercato dei laminati piani del titanio con utilizzo di bramme di acquisto, intende perseguire con questo nuovo progetto i seguenti obiettivi:

- alimentare con bramme di propria produzione gli impianti di laminazione sia a caldo che a freddo che già sono specializzati in questo settore e per questo la localizzazione impiantistica è stata prevista a Terni dove è già stata concentrata anche la produzione di acciai inossidabili, anche in considerazione del fatto che le due linee di produzione, come già accennato, sono complementari e integrative.

. ridurre il costo complessivo di produzione tramite l'utilizzo di un procedimento innovativo e integrato.

. colmare il vuoto oggi esistente in Europa (anche in funzione dell'integrazione europea) dove esistono grosse capacità di rifusione ma limitate capacità produttive di spugna che quindi è quasi totalmente di provenienza extraeuropea.

Il progetto comporta la produzione di titanio metallico per via elettrolitica particolarmente puro partendo dal minerale.

Rispetto ai processi tradizionali i punti di forza del nuovo procedimento elettrolitico sono sintetizzabili in:

- processo in continuo e quindi più assoggettabile ad automazione spinta

- prodotto di maggior purezza e di caratteristiche più costanti
- minor consumo energetico
- maggiore semplicità impiantistica e gestionale.

Ritenendo sia di interesse una breve descrizione tecnica dell'impianto in corso di realizzazione a Terni, che oggi rappresenta la maggiore applicazione industriale del processo elettrolitico, lascio la parola all'ITALIMPIANTI, la quale in questo progetto agisce come "Main Contractor".

# V° MEETING INTERNAZIONALE
# SUL TITANIO

Torino, 9 Novembre 1989

EMANUELE PROFACE

# IMPIANTO DI PRODUZIONE TITANIO IN ITALIA

# INDICE

Allegati:

- Schema a blocchi
- Lay-out

## 1. PREMESSA

Questa descrizione riguarda l'impianto di produzione spugna di titanio elettrolitico da 4200 t/a partendo da rutilo naturale, in corso di progettazione e di realizzazione a Terni.

Della spugna prodotta, una quantità massima pari al 50% ( = 2100 t/a) potrà essere trasformata in lingotti, mentre il resto verrà infustata e venduta.

I lingotti invece verranno utilizzati dall'ILVA di Terni per produrre laminati piani.

L'impianto sorgerà su un'area di circa 42.000 $m^2$, di cui ~ 22.000 coperti e il suo lay-out mostra con maggiore dettaglio le unità di processo e di servizio.

Dallo schema a blocchi si può vedere in maniera semplificata la composizione dell'impianto e le interconnessioni fra le varie unità che lo costituiscono.

## 2. DESCRIZIONE DEL FUNZIONAMENTO

Nella parte "iniziale" (nel senso del flusso) dell'impianto vengono stoccate, manipolate, essiccate e dosate le materie prime solide, che sono rutilo (minerale contenente il 95% di biossido di titanio) e coke di petrolio calcinato.

Lo scarico del rutilo è previsto in fossa da parte di vagoni ferroviari.

Per il coke si prevede un sistema di travaso pneumatico dall'automezzo al silo, mantenendo lo scarico tramite fossa come riserva.

Dallo scarico fino all'utilizzo i materiali solidi vengono stoccati, trattati e movimentati fuori del contatto con l'ambiente esterno per evitare eventuali fuoriuscite di polveri (anche se le sostanze sopra citate non sono tossiche).

Gli stoccaggi previsti sono pari a 420 $m^3$ per il rutilo (~ 1000 t) e a 220 $m^3$ per il coke (~ 170 t).

Le materie prime solide vengono fatte reagire con il cloro per produrre $TiCl_4$ grezzo, con una potenzialità massima di circa 2.16 t/h.

Oltre al $TiCl_4$ nella reazione vengono prodotti altri cloruri dovuti alla reazione del cloro con gli altri ossidi metallici presenti nel rutilo (alluminio, vanadio, ferro, zirconio, ecc.).

Successivamente alla reazione i prodotti vengono a subire vari trattamenti aventi lo scopo di purificare il $TiCl_4$ e di ottenere effluenti pienamente compatibili con i limiti di legge.

Essendo l'impianto di produzione $TiCl_4$ e l'impianto di produzione spugna vicini e strettamente integrati fra loro (in particolare per quanto riguarda il $Cl_2$, che è prodotto nel secondo e riutilizzato completamente nel primo) sono sufficienti limitati stoccaggi di $TiCl_4$ e di $Cl_2$.

Questo fatto rappresenta un aspetto molto valido dal punto di vista ecologico, ed è uno dei punti più qualificanti dell'impianto sotto questo punto di vista.

Il processo elettrolitico per produzione di titanio in "continuo" messo a punto dalla GTT di Torino si svolge in un bagno fuso di cloruro di sodio e si suddivide in 2 fasi: nella prima, detta di "dissoluzione" avviene la riduzione del tetracloruro di Titanio in bicloruro di Titanio, mentre nella seconda denominata "estrazione" vi è l'ulteriore riduzione di quest'ultimo a Titanio metallico, il quale si deposita sui catodi da dove verrà successivamente estratto.

In entrambe le reazioni vi è sviluppo di cloro gassoso il quale viene aspirato e convogliato all'impianto di produzione $TiCl_4$ ove rappresenta uno dei reagenti.

Gli elettrodi immersi nel bagno fuso vengono alimentati con corrente continua che ha lo scopo di rendere possibile la riduzione da tetracloruro di titanio a titanio metallico e di mantenere in fusione il sale per effetto Joule.

Il titanio prodotto, dopo essere stato rimosso dai catodi, viene raffreddato e quindi stoccato, pronto per essere inviato alla successiva operazione di lisciviazione.

La capacità produttiva di spugna elettrolitica di titanio prevista è pari a 4200 t/anno circa su 330 giorni lavorativi (7920 ore/anno), pari cioè a circa 525 kg/h con un consumo di 2160 kg/h di tetracloruro di titanio ed uno sviluppo di cloro di 1635 kg/h.

La produzione viene effettuata in 24 celle, da 525 kg/giorno di titanio ciascuna, riunite a gruppi di 4 in 6 moduli di elettrolisi.

Nel reparto di lisciviazione si procede sostanzialmente alla pulizia del titanio proveniente dalle celle di elettrolisi. All'uscita da queste, infatti, il metallo si presenta in pezzi ricoperti da cristalli di sale (NaCl) inaccettabili nel prodotto finale, che deve risultare puro almeno al 99,6% (norme ASTM).

La spugna di titanio lisciviata (fino a 4200 t/a ~ 12,7 t/d) viene confezionata in fusti oppure trasformata in lingotti.

Fino al 50% della produzione di spugna, nell'ipotesi prevista, può essere trasformata in lingotti.

## 3. ASPETTI ECOLOGICO-AMBIENTALI

Nella progettazione e nella realizzazione dell'impianto si è considerata prioritariamente la tutela della salute e della sicurezza del personale addetto e dell'ambiente urbano e una quota notevole dell'investimento è dedicata a sistemi ed attrezzature di protezione.

Oltre agli aspetti processistici finalizzati alla protezione dell'ambiente (quantità stoccate ridotte al minimo, sistemi chiusi per il trasporto delle materie prime, ecc.) vogliamo citare alcune delle altre protezioni previste.

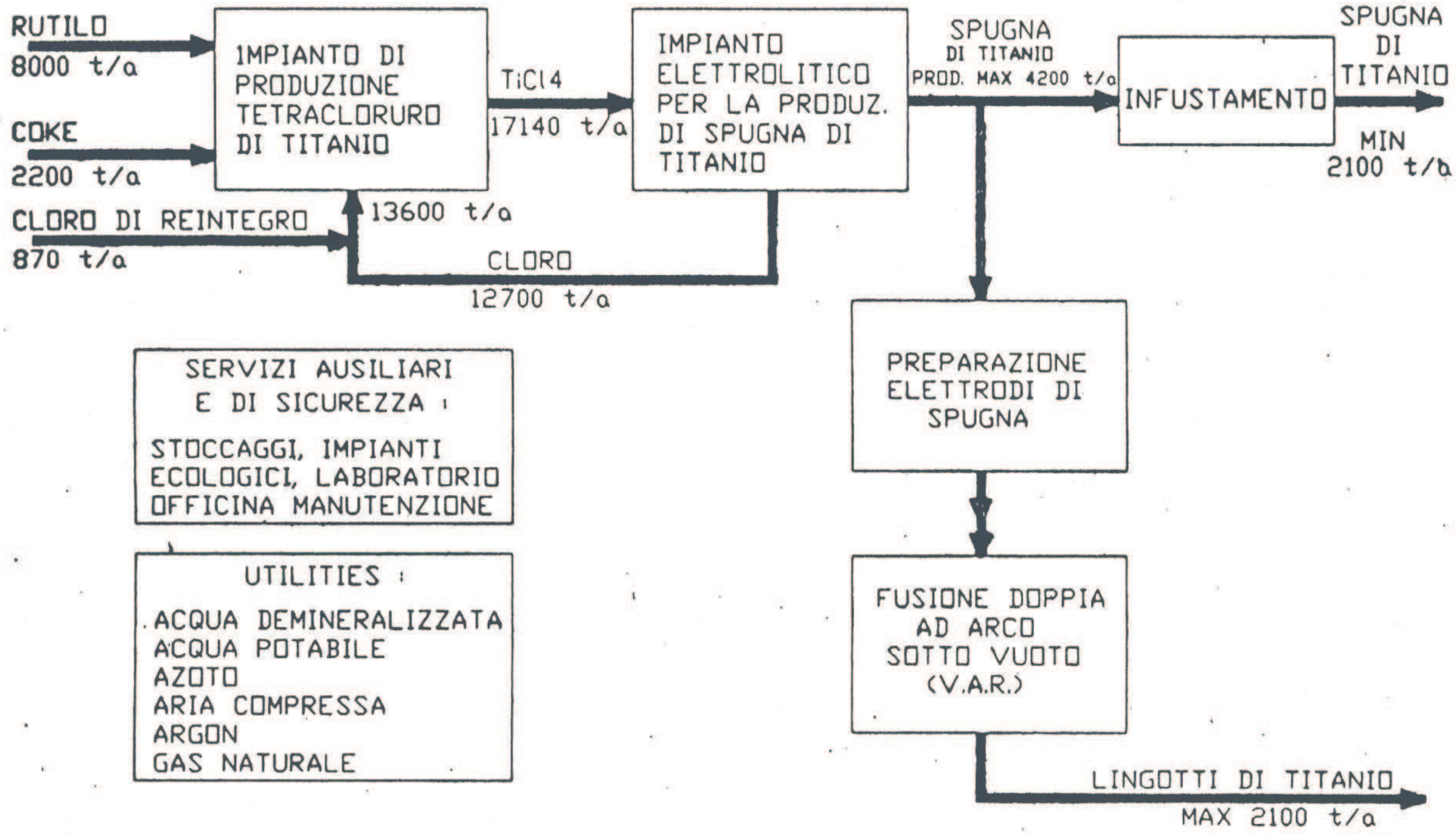
Il cloro prodotto nelle celle elettrolitiche e movimentato fondamentalmente a pressione inferiore o vicina a quella atmosferica, al fine di evitare fuoriuscite accidentali.

I serbatoi di stoccaggio del cloro sono previsti all'interno di un apposito edificio di contenimento mantenuto in depressione, munito di sistemi di rilevamento e collegato ad un impianto di neutralizzazione di eventuali vapori che interviene automaticamente in caso di necessità.

Un secondo impianto di neutralizzazione è previsto per eliminare eventuali tracce di cloro dai prodotti della reazione di produzione del $TiCl_4$, ed è previsto il collegamento con il primo impianto, quale ulteriore sicurezza.

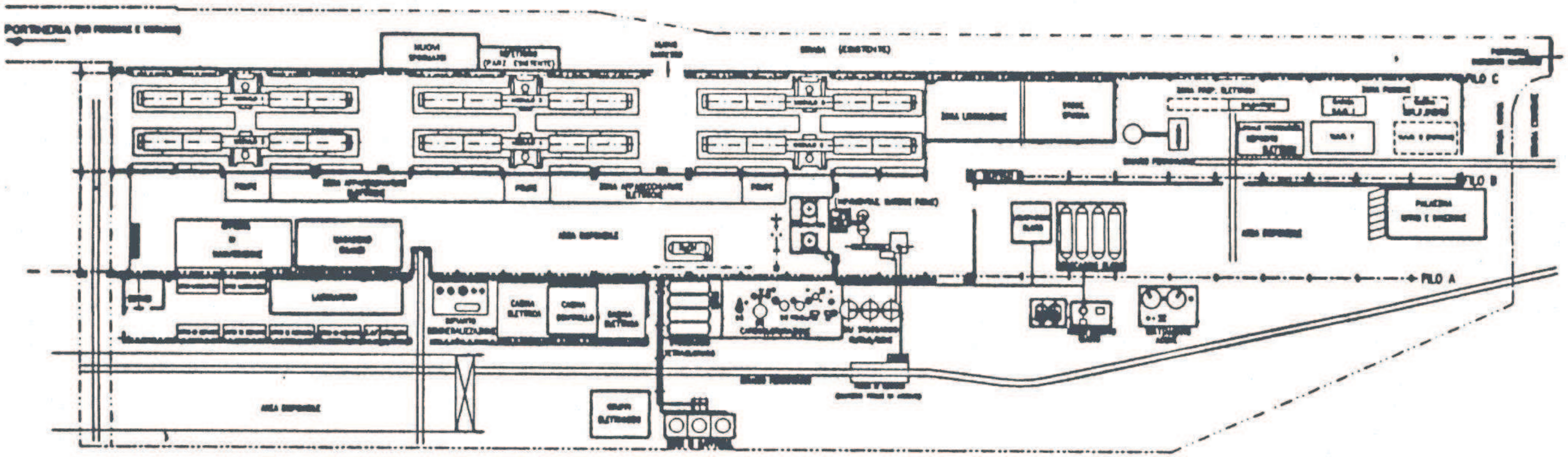
La strumentazione di analisi e di controllo, del tipo più moderno, copre tutte le unità dell'impianto e permette in ogni momento di intervenire con la massima affidabilità.

In definitiva riteniamo che questo progetto, all'avanguardia dal punto di vista tecnologico, lo sarà anche dal punto di vista della salvaguardia degli aspetti ecologici ed ambientali rappresentando, ci auguriamo, un punto di riferimento per future iniziative industriali.



ITALIMPIANTI / GENOVA

TITANIA / TERNI
IMPIANTO PRODUZIONE TITANIO DA 4200 t/a
SCHEMA A BLOCCHI



TITANIA / TERNI
IMPIANTO PRODUZIONE TITANIO DA 4200 t/a
LAY - OUT

ITALIMPIANTI / GENOVA

Stan R. Seagle
RMI Company - U.S.A.

# TITANIUM TECHNOLOGY FORECAST

## 1 - INTRODUCTION

Titanium usage continues to grow being spurred by an expanding commercial aerospace industry and increased requirements in non-aerospace applications. Currently, non-aerospace usage is approximately 20% of USA consumption. The rapid growth rate of this market segment suggests that the non-aerospace usage of titanium will be a larger portion of total market in the 1990s.

High specific strength (strength/density) to 1000 F is the key property utilized in applying titanium alloys in aerospace applications. In non-aerospace use, titanium's excellent corrosion resistance is often the critical, and most important characteristic. These two properties, specific strength and corrosion resistance, differentiate titanium from other materials and account for nearly all the titanium applications.

Titanium, a relatively new commercial metal, has demonstrated excellent performance in aerospace to moderately elevated temperatures and outstanding corrosion resistance in neutral and mildly acidic chloride environments. As we move into the 1990s, new titanium alloys are expected to be used at higher temperatures, at higher strength levels and in more aggressive environments. In addition, the gas turbine industry will require continually improved quality to enhance both performance and safety. Specific background on these expected advances in alloy and process technology are discussed below.

## 2 - HIGH TEMPERATURE ALLOYS

Figure 1 contains elevated temperature stress-rupture data on both current and developmental titanium base alloys. Ti-6242 is the most advanced commercial alloy and used extensively in the U.S.A for the high temperature compressor portions of gas turbines.
The maximum design temperature for this alloy is about 1000 F. More recently, the temperature capability of titanium has been increased to about 1150 F through the development of IMI834 by IMI in England and Ti-1100 by Timet in U.S.A.. The IMI834 is being used in modest quantities in new Rolls Royce engines while the Ti-1100 is being evaluated by U.S.A. engine producers for potential use. As the applications temperature exceeds about 1050 to 1100 F, surface oxidation of titanium alloys becomes to develop suitable coatings that could be used with

confidence to prevent oxidation. The marginal improvement in temperature capability over existing titanium alloys (150F) and the potential need for coatings to prevent oxidation, could present a significant barrier to obtain the necessary expensive verification and approval required for gas turbine applications in the U.S.A..

The intermetallic compounds ($Ti_3Al$ ($\alpha 2$) and TiAl ($\delta$) have appreciable appeal because of their very high elevated temperature strength and low density. The $Ti_3Al$ alloy has attractive strength to 1350 F while the TiAl is expected to be used as high as 1700 F. The low ductility (2 to 5%) of $Ti_3Al$ and even lower ductility of TiAl (<2%) has presented problems in design, in manufacturing components and in producing sizable quantities of mill products. Current programs in modifying the alloy composition and processing research indicate acceptable ductility can be achieved in $Ti_3Al$ type alloy. Recently, titanium mill manufacturers have produced mill products including .020"x36"x96" sheet form production size ingots. Progress on TiAl has not been as encouraging and only small quantities of material are available from laboratory-type processing. Both intermetallic alloy systems are of significant interest in the National Aerospace Plane (NASP) Program. The rate of development and application of these titanium intermetallics will depend on NASP funding effort. Without the NASP support, however, some engine applications for $Ti_3Al$ type alloy is still expected in the 1990s.

The high temperature strength potential of titanium alloys is greatly enhanced when combined with silicon carbide fibres to form a metal matrix composite. Many issues must be resolved before extensive use occurs. Some of the well-known issues are directional properties, low damage tolerance, non-destructive inspection problems and high cost. In addition, suitable methods of producing these metal matrix composites must be developed. The sandwich method of roll-fiber-foil is not attractive because of the difficulty of producing foil of the matrix alloys. A plasma spray process such as developed by G.E. Aircraft Engine Group appears a more likely method of fabrication. Because of the numerous problems in production, only small quantities of titanium metal matrix composites are expected to enter application in the next decade.

## 3 - HIGH SPECIFIC STRENGTH ALLOYS

Titanium alloys are generally creep limited above approximately 600 F. Below this temperature specific ultimate strength, fatigue and toughness are all major design considerations. Annealed Ti-6Al-4V (Ti64) has been the dominate alloy since the 1950s at temperature below 800 F. Although the strength of this annealed alloy (130 ksi UTS) is very competitive with other metals, there has been little enthusiasm to utilize the high strength capability (>150 ksi UTS) of heat treatable titanium alloys. As builders of airframe and engines attempt to design and produce more efficient structures, higher strength alloys will be used. Engine manufacturers already utilize heat treatable alloys such as Ti-6246 and Ti-17 at temperatures in the 500 F to 800 F range. However, use of high strength titanium alloys is not significant in airframe structures. Advanced military airframes of the 1990s may utilize new high strength high toughness alloys such as Ti62222 (Ti-6Al-2Sn-2Z-2Mo-2Cr-0.25Si) shown in Figure 2. This alloy allows the use of higher strengths without a significant change in fracture toughness.

Titanium alloy springs are one of the few high strength applications in airframes. Titanium alloys with a high specific strength and low modulus, is an ideal spring material (Figure 3). Beta-C$^{TM}$ is utilized as springs in airframes at 200 ksi ultimate strength. Modest quantities are now being used, but the amount is expected to grow because of the significant weight savings (50%) and design compactness.

The high strength capability of beta type titanium alloys also is expected to be exploited for use in high strength castings. Figure 4 shows typical properties of the beta alloys Ti-15-333 and Beta-C$^{TM}$.These properties are comparable to high strength steels such as 17-4PH. Currently Ti-64 castings are used extensively in non critical components of the gas turbine engine. Use of the lower strength Ti-64 castings in airframes is starting to occur and the use of the high strength beta type alloys is now a consideration for application in the 1990s.

## 4 - CORROSION APPLICATION

Engineers in the chemical process industries began applying titanium in the early 1960s. At the same time, titanium's unique electrochemical characteristics revolutionized the chlor/alkali industry through the use of precious metal-coated, dimensionally-stable titanium anodes.
From this start, titanium quickly expanded into many distinct market areas such as chemical, power, petrochemical, refinery and pulp and paper. Future non aerospace growth is expected to occur in 1990s in energy extraction, biomedical, concrete re-enforcement protection, electronic, automotive, marine and environmental applications.

Many, if not most, of the current applications are based on commercially pure titanium, a moderately low strength metal. Titanium ASTM Grade 7 (Ti-0.2Pd) and more recently ASTM Grade 12 (Ti-0.3Mo-0.8Ni) have expanded the use of titanium because of their improved corrosion performance in reducing acidic chloride environments. Unfortunately, both alloys have only moderate tensile strength, which limits their application in many industrial areas particularly at elevated temperatures. Recently a commercial, high strength beta titanium alloy, Beta-C$^{TM}$, was found to possess comparable corrosion resistance to Grade 12. This finding, unique because the alloy is heat-treatable to high strength with exceptional corrosion resistance, will fill a void in several markets, particularly in energy extraction where high temperature strength combined with corrosion resistance in slightly acidic brines containing $H_2S$ is desired.

For pressure vessel application, only commercially pure titanium and a few low-strength titanium alloys are ASME Boiler Code approved. Currently, the industry is in the process of qualifying Ti-3Al-2.5V (ASTM Grade 9). Figure 5 illustrates the design strength advantage of this alloy when compared with other titanium and nickel-base alloys.
The alloys are compared on a design stress-to-density ratio, which reflect weight efficiency of a structure and therefore, is directly related to cost per pound. After code approval is received for Ti-3Al-2.5V in 1990, these property advantages, combined with excellent mill producibility, good fabricability and good corrosion resistance offer new opportunities in design of elevated temperature pressure vessel equipment.

The development of high-strength alloys for pressure vessels and for reducing chloride environments will broaden the applicability of titanium. Figure 6 summarizes the general corrosion and strength behaviour of titanium alloys. Higher elevated temperature strength, coupled with excellent corrosion resistance in oxidizing and moderately reducing environments results in a metal system with a broad range of applications.

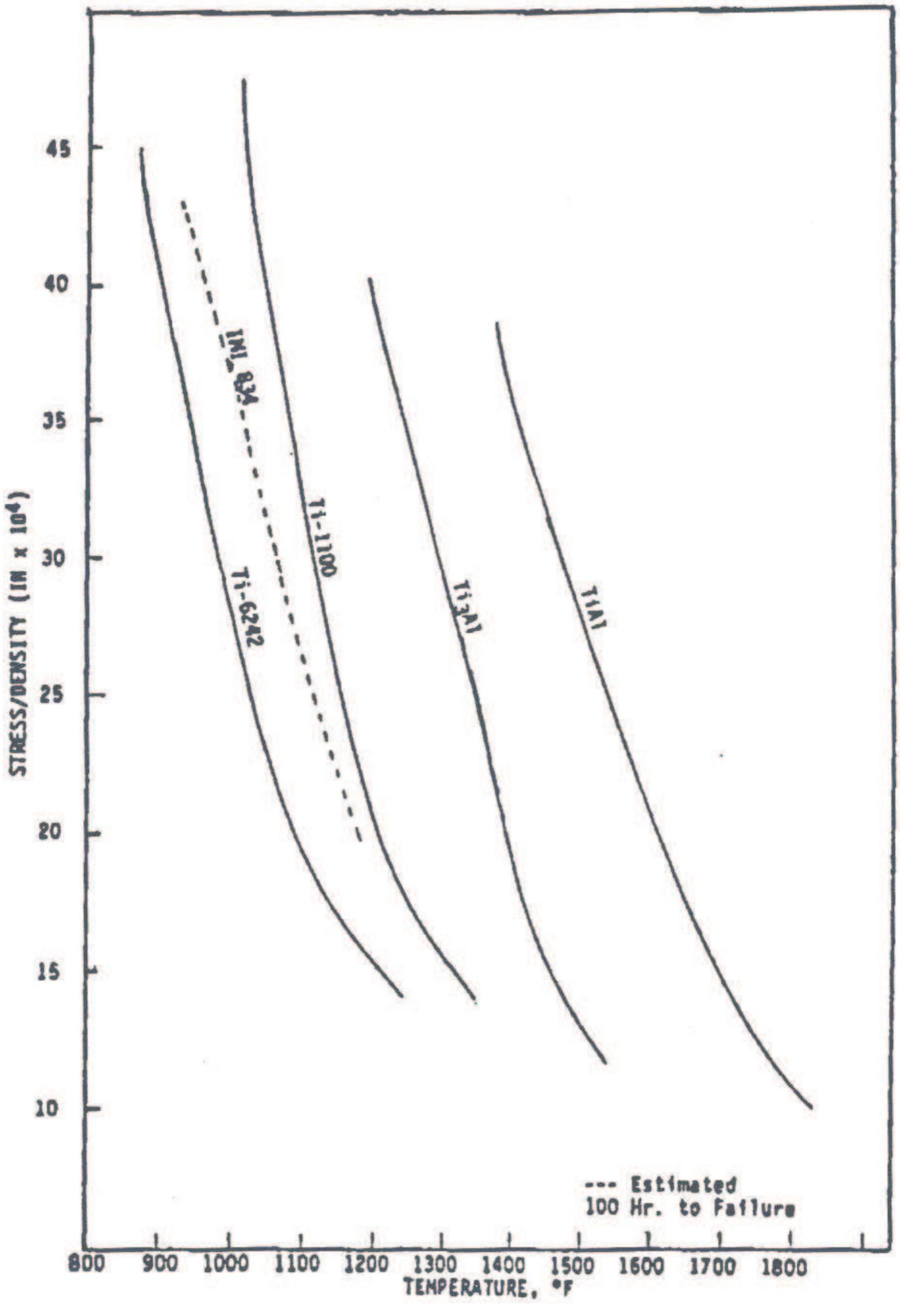
## 5 - PROCESS IMPROVEMENTS

Aerospace applications, particularly jet engines, require continually improved quality. The most bothersome and persistent defect associated with titanium products has been a high melting point interstitially rich area commonly called LDI or Type I. The defect, being extremely hard, can act as a nucleation site for premature failure. Although the incidence rate for such a defect has decreased significantly in the past decade, the defect can still occur. New technology scheduled for major implementation in the early 1990s, should solve this nagging issue. The process consists of replacing a vacuum arc melting operation with a hearth melting operation. This newer process will either dissolve the defect or allow the defect to settle innocuously in the hearth skull. Two electron beam hearth and one plasma hearth furnaces are now operating in the U.S.A.

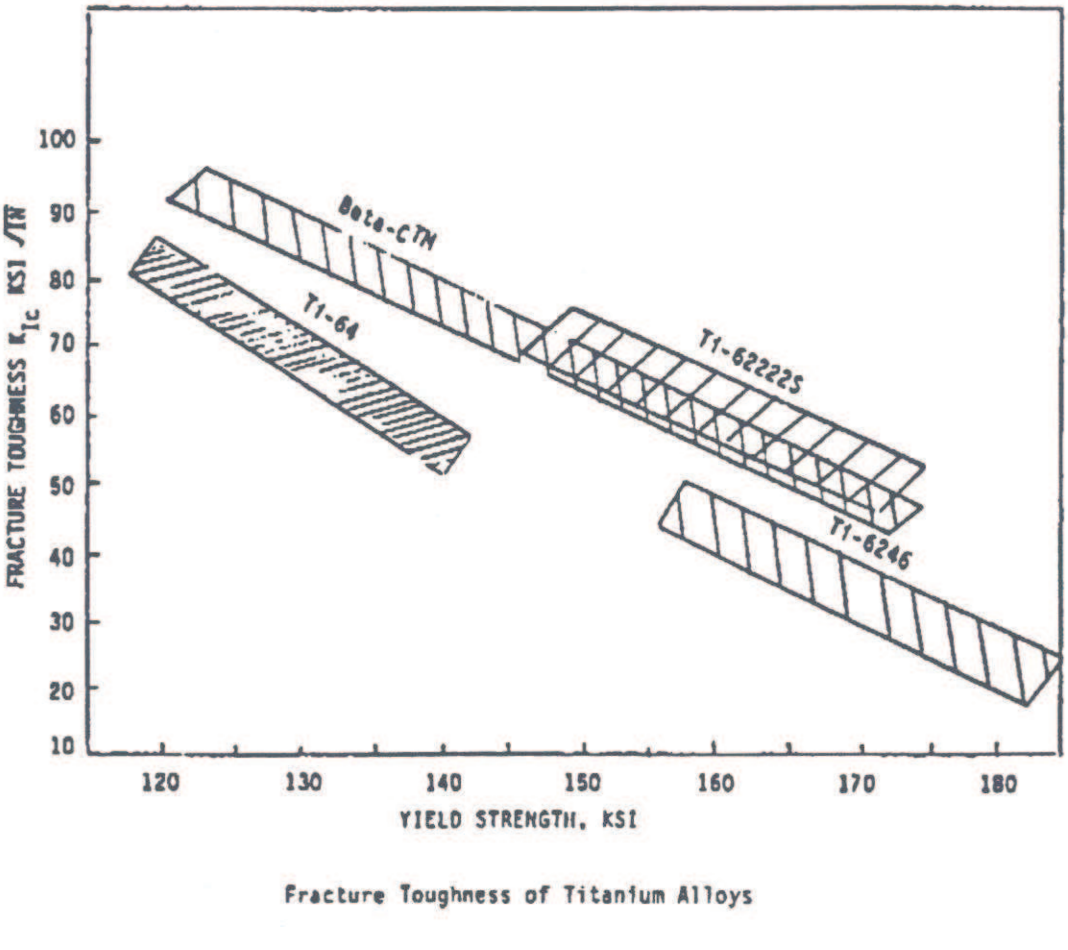
G.T.T., an engineering company in Turin, Italy has developed a new process for the electrolytic production of titanium sponge. The process produces a very high purity sponge containing both low oxygen and low residual metallics. In addition, the volatile residuals are about 50% of the best sponge now commercially available. This low volatile content will be desirable for the developing plasma and electron-beam melting processes. A large demonstration unit (300.000 lbs per year) has been started up this year and is scheduled for experimental operation at RMI Company in Ashtabula, Ohio in early 1990.

## 6 - SUMMARY

The 1990s will bring new challenges in the form of developing mew markets and improving quality. In aerospace, new applications will result from improved high temperature alloys for engine applications and new high strength alloys for airframe use. The industrial market growth will occur due to increased information on titanium's corrosion resistance and the availability of new and improved alloys.



Stress Rupture of Titanium Alloys



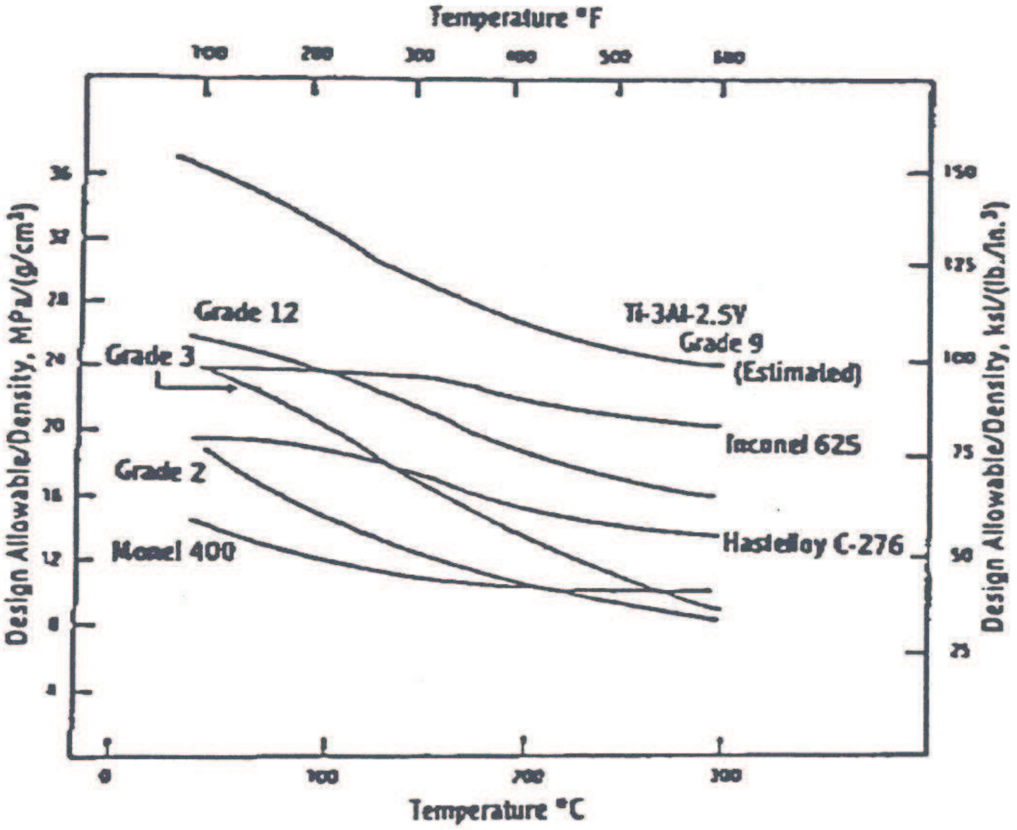
Fracture Toughness of Titanium Alloys

Equivalent Designs in Springs of Titanium and Steel. Titanium is 55% of Steel Weight

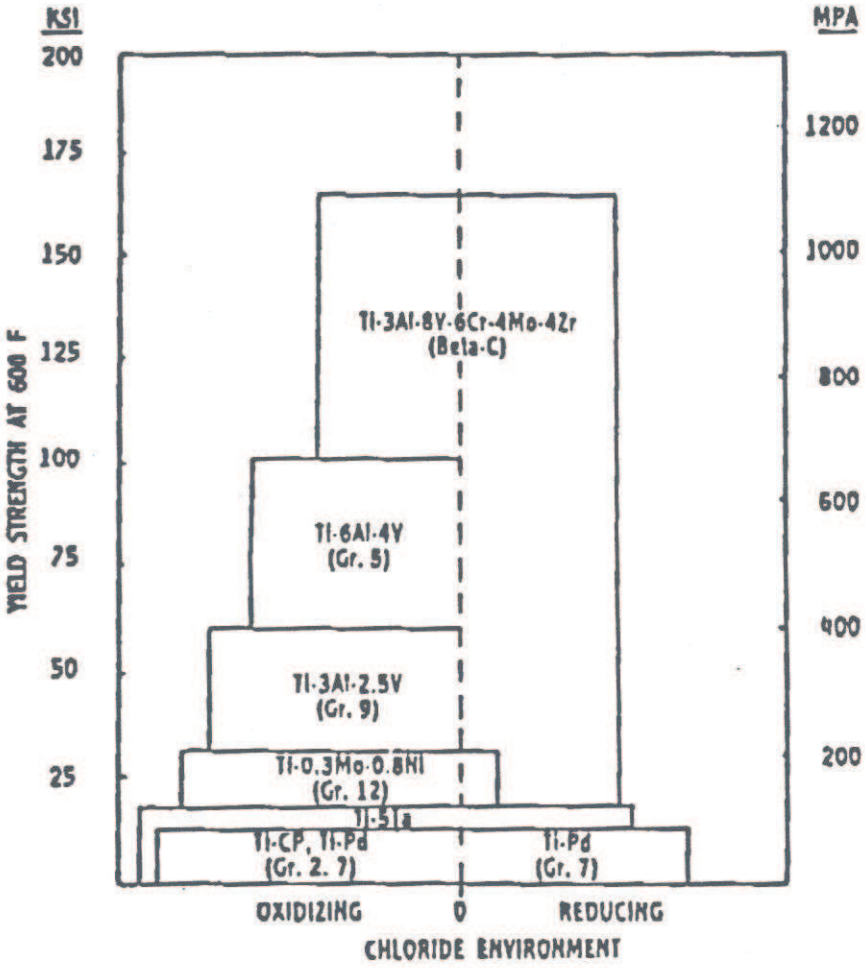
## ROOM TEMPERATURE TENSILE PROPERTIES OF TITANIUM ALLOY CASTINGS

| ALLOY | UTS Ksi | YS Rsi | EL % | RA % |
|---|---|---|---|---|
| Ti-64 | 135 | 124 | 10 | 15 |
| Ti-6246 | 195 | 184 | 2 | 3 |
| Beta-C$^{TM}$ | 193 | 180 | 7 | 12 |
| Ti-15-333 | 163 | 151 | 7 | 13 |

Source: Precision Castparts Corporation



Structural Efficiency
of Titanium and Nickel Alloys



Yield Strength vs. Corrosion Resistance For Titanium Alloys

# AUSTRALIA'S DOMINANCE
# IN THE
# TITANIFEROUS FEEDSTOCKS MARKET

## THE COOLJARLOO PROJECT

AUTHORS: R J WILDE*
M C ACKLAND**

NOVEMBER,1989

* Managing Director, Minproc Holdings Limited
**Director, Minproc Holdings Limited

## SYNOPSIS

Australia is the largest supplier in the world of titaniferous feedstocks, exporting the majority of ilmenite, rutile and synthetic rutile production to Europe, the United States of America and Asia.

This paper describes the forces which drive the market for titaniferous material, the titanium dioxide pigment production processes, the changes in future pigment manufacturing methods and the shift this will cause in the feedstocks markets.

The importance of the production of titanium tetrachloride as an intermediate feedstock for pigment and titanium metal production is discussed.

Minproc Holding Limited and Kerr-McGee Chemical Corporation are developing the world's first fully integrated "mine to pigment" project in Western Australia. The Cooljarloo project has more than 24 years supply of titaniferrous minerals available for processing into pigment, synthetic rutile titanium metal and other associated products.

# AUSTRALIA'S DOMINANCE IN THE TITANIFERROUS FEEDSTOCKS MARKET
# THE COOLJARLOO PROJECT

## 1.0 INTRODUCTION

The mineral sands industry worldwide is relatively young. Demand for titaniferous raw materials increased rapidly with the outbreak of World War II and the inception of most pigment and titanium metal production can be traced back to this world event. The cessation cf hostility allowed the mineral sands business to develop, having emerged during the war from its embryonic 1930's form to the current general structure.

Australia's mineral sands industry, which had been intermittent in operation from its early years in the 1870's, matured during World War II and in 1944, the Commonwealth of Australia placed a strategic ban on the export of mineral sands concentrates. The market weakened in post war years, recovered in 1950 and has expanded since that time. Australia is the major producer of mineral sands in the western world and accounts for more than 60% of titaniferous minerals in the world today.

This paper will not discuss non-titaniferous material but the associated zircon which is generally recovered with Australian mineral sands concentrates is an important product, as is monazite, for rare earth extraction.

The Cooljarloo project is the sole vertically integrated "mining to pigment project" anywhere in the western world.

Some details of the Cooljarloo project will be discussed in conclusion of this paper to illustrate a fully integrated mining, beneficiating, upgrading and processing venture in titaniferous materials.

Figure 1 depicts the industry structure and shows the varying stages of processing of titaniferous materials and the end uses of these products.

Ilmenite production forms the basin of the majority of titaniferous feedstocks that are consumed by synthetic rutile plants of direct-feed, sulphate pigment plants. Synthetic rutile, natural rutile and a higher grade slag are used for chloride process pigment production.

Hard rock mined ilmenite is treated via a slagging process which produces a generally lower grade titanium dioxide product.

It is significant to titanium metal production to recognize the output of titanium tetrachloride as an intermediate step in the production of high purity titanium dioxide pigment. Titanium tetrachloride is the primary feed for the manufacture of titanium metal by the Kroll, Hunter or Ginatta processes.

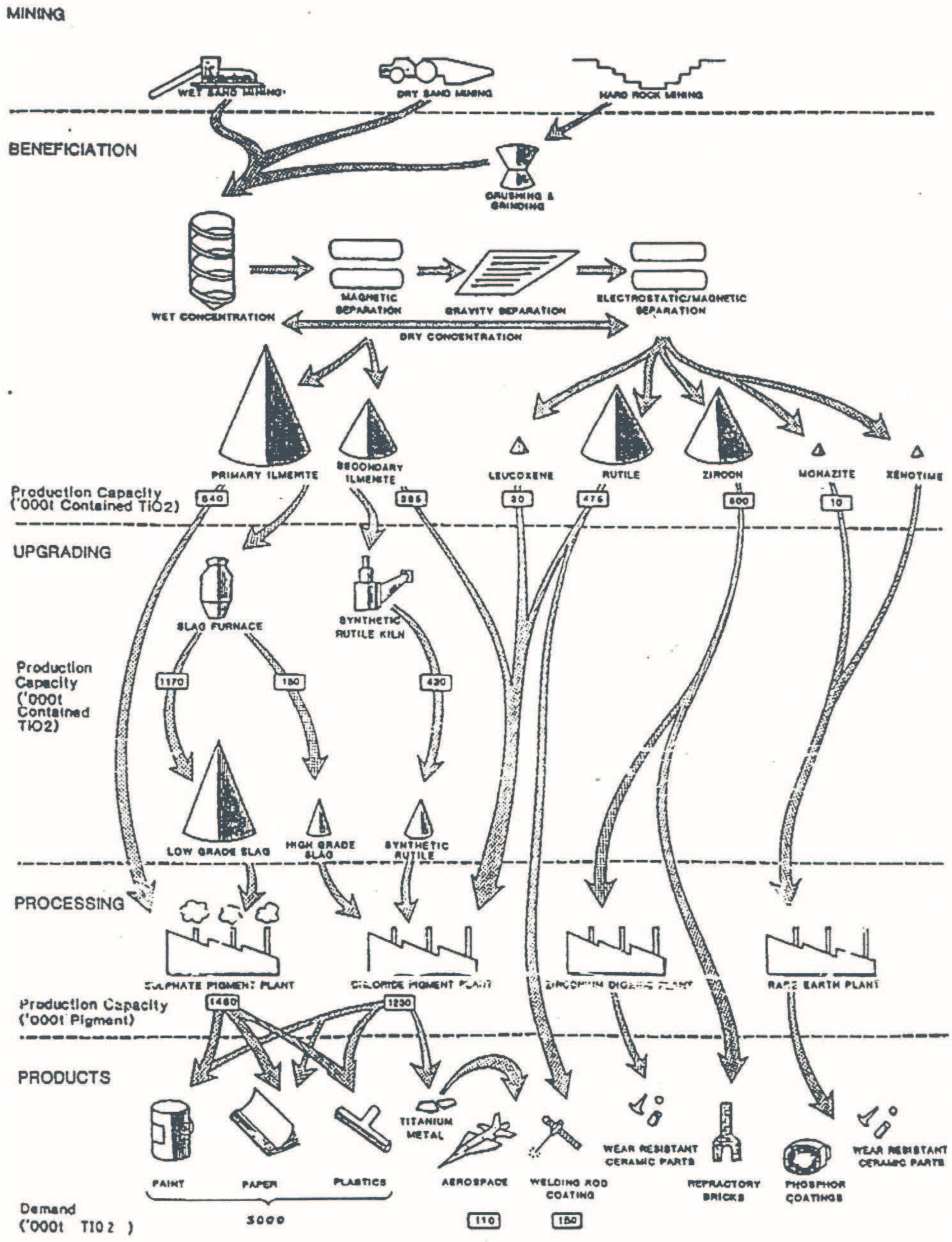


Figure 1. Mineral Sand Processing Flow Sheet

## 2.0 THE HEAVY MINERAL COMMODITIES

Heavy minerals are mined and beneficiated, mostly from unconsolidated beach and dune sand, but also from hard rock deposits. The rutile, ilmenite and zircon products and by-product monazite and xenotime are processed to extract their metal oxides which are consumed in a multitude of end uses mainly associated with computors, communications and aerospace industries.

### 2.1 Market Model

Figure 1 illustrates the general titaniferous material flow which is driven by the following forces:

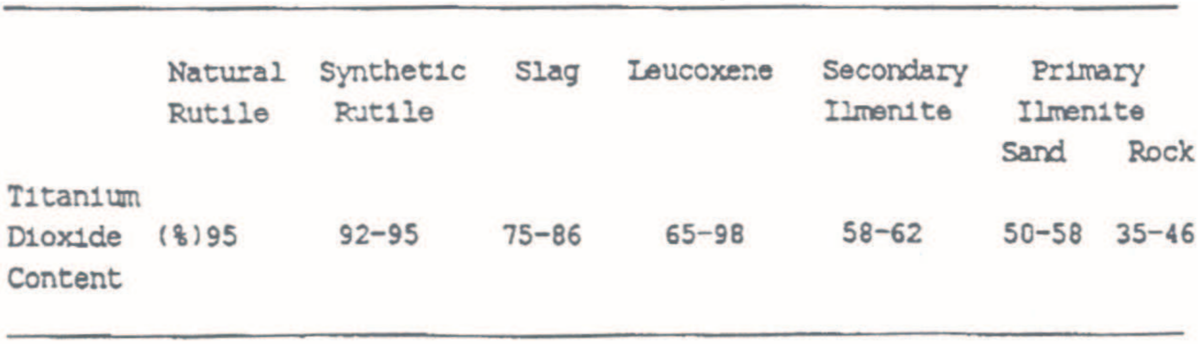
* The demand for paint, paper and plastics essentially determines the demand for titanium dioxide pigment.
  - 93% of pigment is consumed in these markets.

* Pigment demand determines the demand for titanium bearing minerals rutile and ilmenite (in its various forms).
  - 92% of titanium is consumed in the pigment form
  - 4% in the form of rutile and high titanium bearing mineral mixtures
  - 3% as titanium metal.

* The demand for rutile and ilmenite determines the supply of zircon and rare earth oxide bearing monazite and xenotime.

* The preference for different titanium bearing heavy minerals is in part dependent on their titanium dioxide content. Table 1 shows that natural rutile has the highest titanium dioxide content while primary ilmenite has the lowest. Between these two end members lies a range of products derived from ilmenite. Secondary ilmenite and leucoxene represent naturally upgraded derivatives of primary ilmenite while synthetic rutile and slag are manufactured from secondary ilmenite and primary ilmenite respectively.

Table 1
Titanium Dioxide Bearing Minerals



| | Natural Rutile | Synthetic Rutile | Slag | Leucoxene | Secondary Ilmenite | Primary Ilmenite | |
|---|---|---|---|---|---|---|---|
| | | | | | | Sand | Rock |
| Titanium Dioxide Content | (%)95 | 92-95 | 75-86 | 65-98 | 58-62 | 50-58 | 35-46 |

## 2.2 Market Segments

This simplified market model markets for example, the quality and mix of heavy minerals are often as important as deposit grade in determining the economics of mining and hence mineral supply. Some heavy mineral producers further segment supply by upgrading the quality of their ilmenites to either slag or synthetic rutile (see Figure 1).

The demand for "upgraded ilmenites" and other titanium bearing heavy minerals, while generally governed by the demand for titanium dioxide pigment, is also determined by the type of pigment production process. For example, pigment production using the chloride process depends on the availability of high grade titaniferous bearing heavy minerals while the sulphate process uses lower grade feedstocks. In addition, a variant on the chloride process developed by Du Pont uses a blend of high and low grade titaniferous minerals.

The various market segments are identified in Figure 2 for the chloride and sulphate pigment production processes. Slag is now the most important raw material for plants using the sulphate process while synthetic rutile represents the most significant feedstock for chloride plants. Secondary ilmenite is also an important raw material for chloride plants, however its use is restricted to the Du Pont process.

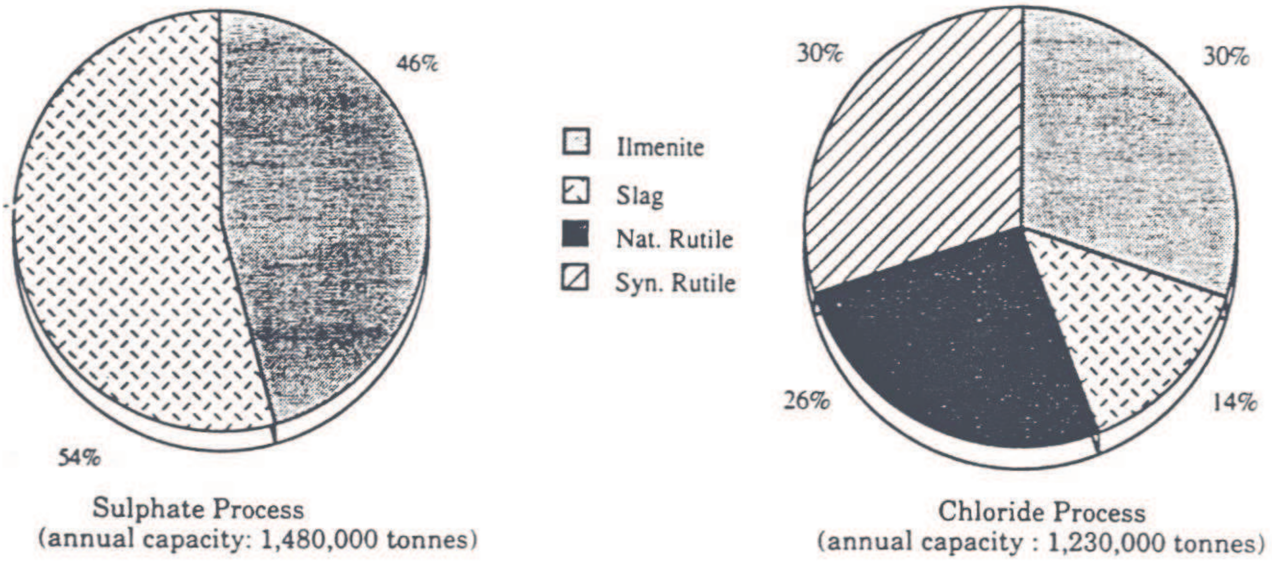


Figure 2. Titanium Bearing Mineral Consumption By Process, 1988
(Percentages based on recoverable titanium dioxide).

## 2.3 Titaniferous Feedstocks For Sulphate Process Pigment Plants

While titanium dioxide content has a strong bearing on the choice of raw material there are several other equally important factors. In the case of pigment plants using the sulphate process, primary ilmenite is an ideal feed because of its relatively large surface area. However, slag now supplies 54% of this market and will increase its share for the following reasons.

- Supplies of good quality primary ilmenite are declining.

- Slag is the only suitable alternative to primary ilmenite as:

  - secondary ilmenite can not be processed due to its low surface area.
  - synthetic rutile can not be processed because it is insoluble in sulphuric acid.

- Slag reduces solid waste production and increases the plant's titanium dioxide capacity. It therefore allows sulphate plant operators to:

  - comply with new environmental standards, particularly in Europe and Japan.
  - reduce unit operating costs.

While these arguments present an appealing case for increasing slag use, each plant has to balance these benefits against the much higher cost of slag, compared with primary ilmenite (see Figure 3).

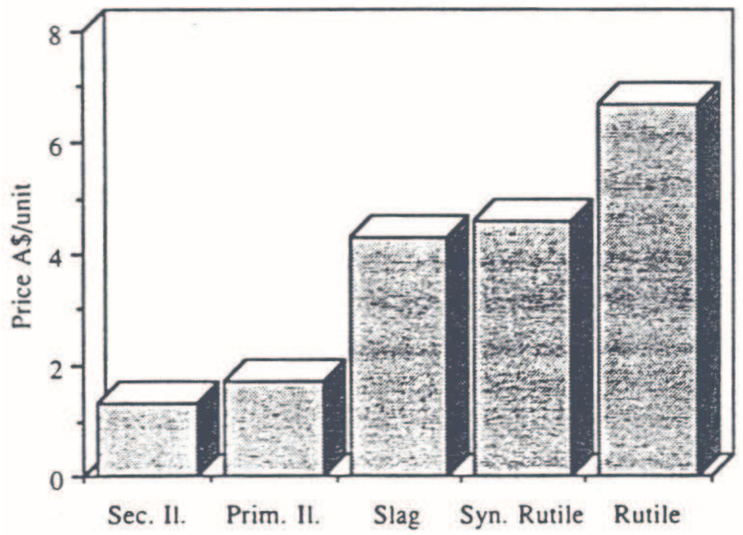


Figure 3. Cost Per Titanium Dioxide Unit of Raw Materials

## 2.4 Titaniferous Feedstocks

Pigment plants using the chloride process are also adjusting their feedstock requirements to use a greater proportion of synthetic rutile. These adjustments are occurring for the reasons listed below.

* The supply of natural rutile is static and pigment producers are faced with greater competition for this raw material from the welding rod market.

* Synthetic rutile is cheaper than rutile and has a higher titanium content than slag (see Figure 3).

* High grade slags (85%+ titanium dioxide) have not achieved a high market acceptance. This is largely because alkalis in the slag reduce the recovery of titanium dioxide and because additional capital expenditure is required before pigment plants can handle slag.

* Slag producers are also experiencing some difficulty in expanding their production of high grade material. South Africa produces a large amount of undersized slag during the crushing process which is unsuitable for chloride process pigment production. Therefore it is faced with the difficult task of reducing the amount of undersized material if it is to increase capacity.

The chloride process plants, based on Du Pont technology, are also likely to use more synthetic rutile in the future. At the present time they are heavily dependent on secondary ilmenite which is increasingly being consumed in the production of synthetic rutile. There is also an ever present threat of tighter waste disposal standards in the United States which, if they eventuate, would force Du Pont to use higher grade feedstocks.

Pigment manufacturers experience problems with low titanium oxide feedstocks, as the iron must ultimately be rejected from the process and be disposed of in an environmentally acceptable manner. The Cooljarloo ilmenite has lower iron content and produces comparatively minimal waste in the upgrading process to synthetic rutile. All neutralized waste produced will be buried in the Cooljarloo mining pit and the areas will be progressively rehabilitated as mining and production proceed.

In the full integration of titaniferous materials processing, it is significant that the chloride process is in effect the starting process for metal production, as an intermediate product $TiCl_4$ is produced. Sulphate process intermediates are not utilized for metal production.

# 3.0 WORLD PIGMENT CAPACITY

## 3.1 Chloride vs Sulphate Process

The trend toward the chloride process is easily understood if the two processes are compared on the basis of waste production, process efficiency and product quality. Pigment capacity by process is shown in Figure 4.

| Sulphate Process | Chloride Process |
|---|---|
| Using Primary ilmenite as the main feedstock creates 3 to 4 tonnes of liquid acid and solid copperas (iron sulphate) waste per tonne of pigment. | Solid waste is not a problem and the main by product, chlorine, is recycled. (Although the Du Pont process produces significant amounts of liquid ferric chloride waste which is pumped into disposal wells). |
| The conversion efficiency is 85 to 90% | The conversion efficiency is 95% (The Du Pont process has a 92% efficiency rating). |
| Product quality is affected by the production of both rutile and anatase forms of pigment. | Product quality is maintained at a high level with the production of rutile grade pigment only. |

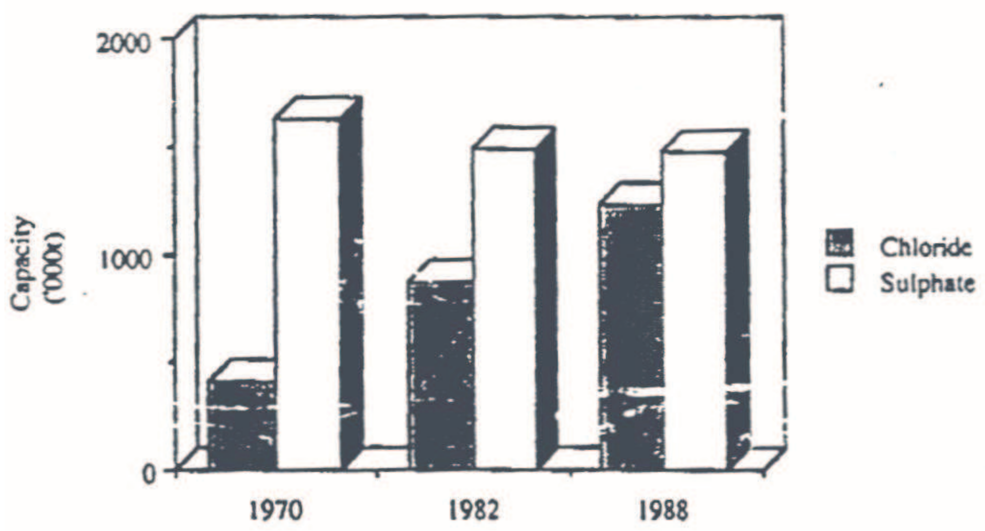


Figure 4. Pigment Capacity by Process.

Chloride process capacity should exceed sulphate process capacity by 1995 because of environmental and cost factors.

### 3.2 Regional Pigment Capacity

The heavy dependence of Western Europe on sulphate process pigment production is seen in Figure 5.

The European Economic Community may see a more rapid move to modify or even close sulphate based capacity in Western Europe or convert it to the chloride process. In Japan, the authorities are also tak1ng a tough line with little new capacity permitted unless it replaces sulphate process pigment plants.

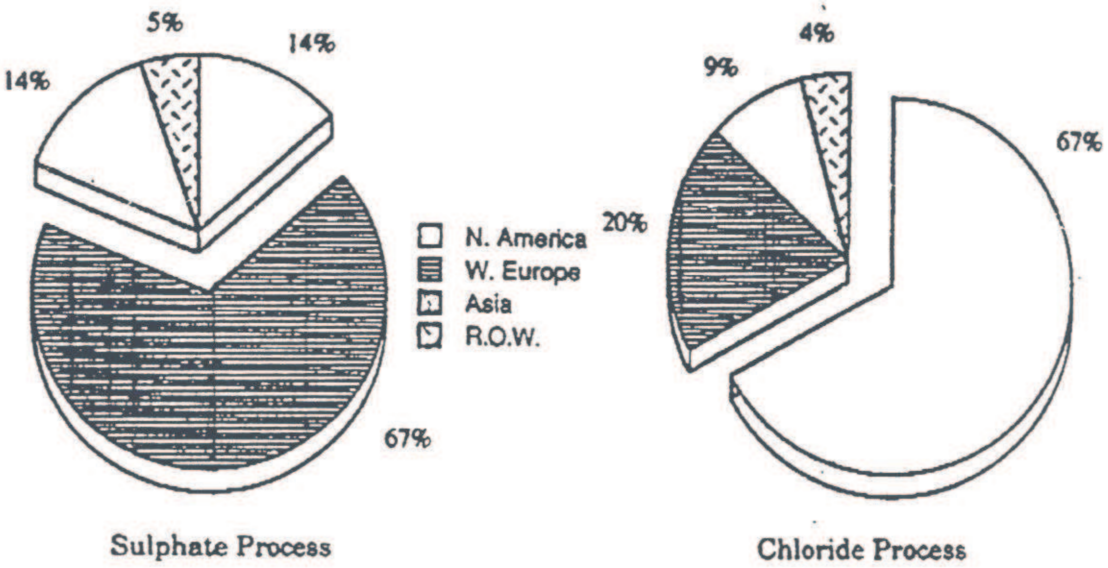


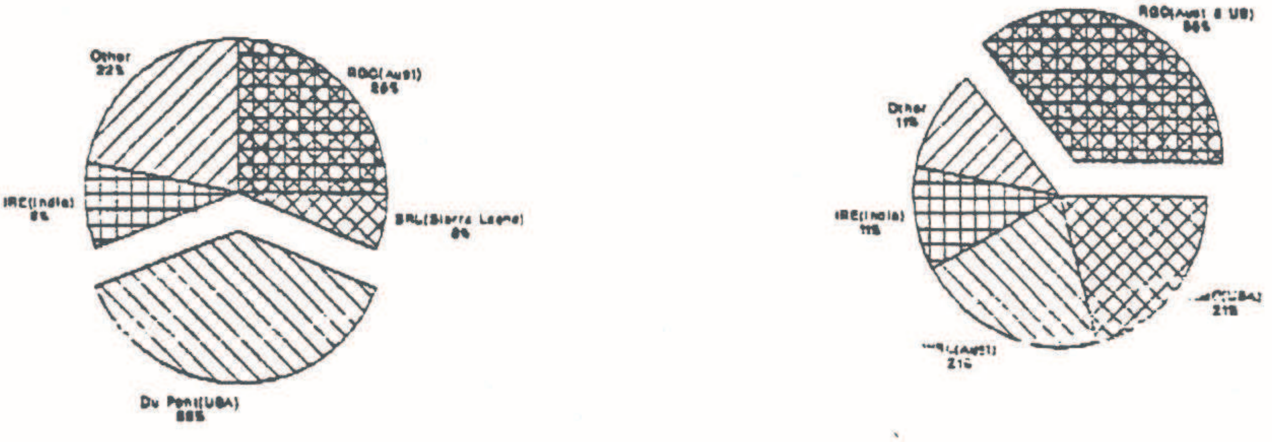
Figure 5. Pigment Capacity By Region, 1988

## 4.0 WORLD TITANIFEROUS FEEDSTOCK PRODUCTION

Australia dominates the world supply of high titanium dioxide feedstocks with major production coming from Renison Goldfields, Consolidated Rutile and Westralian Sands.

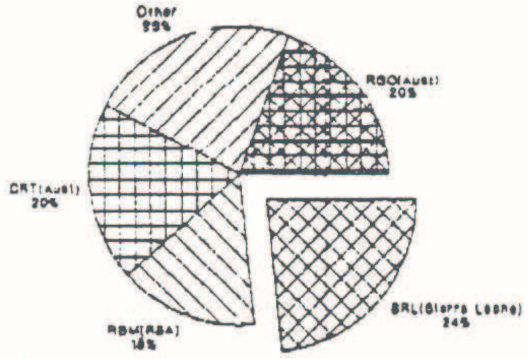
### 4.1 Feedstock Supplies to Chloride Process Pigment Plant

Renison is the world's major supplier to chloride process pigment plants. As Figure 6 shows, Renison Goldfields supplies 25% of the world's secondary ilmenite and 36% of the world's synthetic rutile. The Company is also a major supplier of natural rutile, sharing this position with Consolidated Rutile, Sierra Rutile (SRL) and Richards Bay Minerals (RBM). Pigment producers, Du Pont, SCM and Kerr-McGee (KMC) have large amounts of tied production of secondary ilmenite and synthetic rutile.



Secondary Ilmenite for Chlorination
(annual capacity 705,000 tonnes)
TIO2 Units: 490,000 tonnes

Synthetic Rutile
(annual capacity. 430,000 tonnes)
TIO2 Units: 380,000 tonnes



Rutile
(annual capacity. 452,000 tonnes)
TiO2 Units: 423,000 tonnes

Figure 6. Feedstock Suppliers to Chloride Process Pigment Plants.

### 4.2 Feedstock Suppliers to Sulphate Process Pigment Plants

The supply of titanium dioxide feedstocks to pigment plants using the sulphate process is dominated by the slag producers (see Figure 7). QIT and Richards Bay Minerals share 88% of the slag market while NL Industries is the main supplier of primary ilmenite from its hard rock mine at Tellnes in Norway. Australian mineral sand producers, Westralian Sands, Cable Sands and Renison Goldfields are also significant suppliers of primary ilmenite.

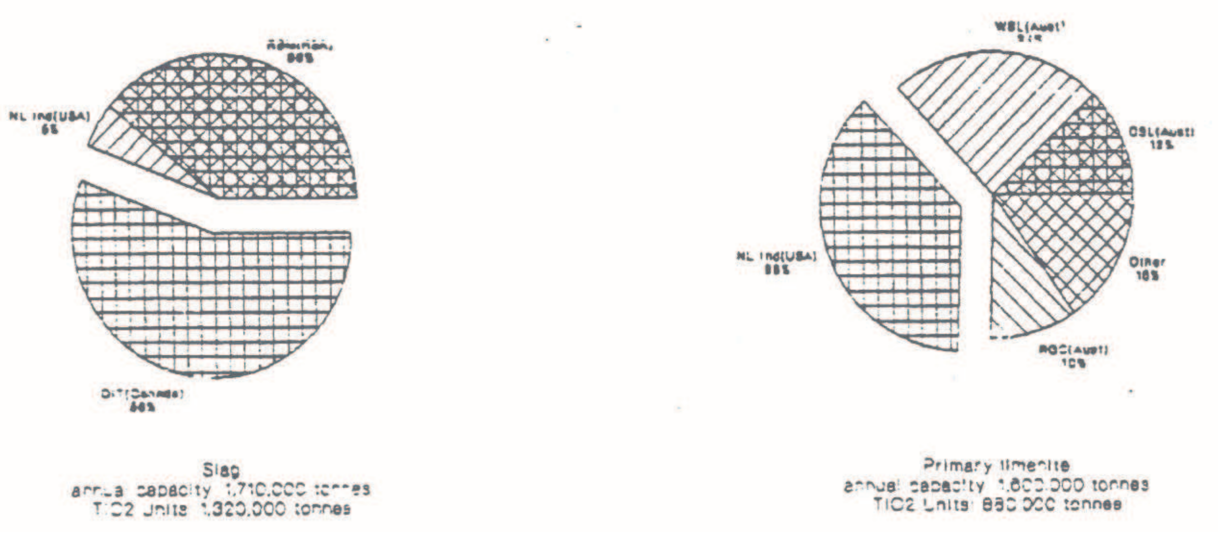
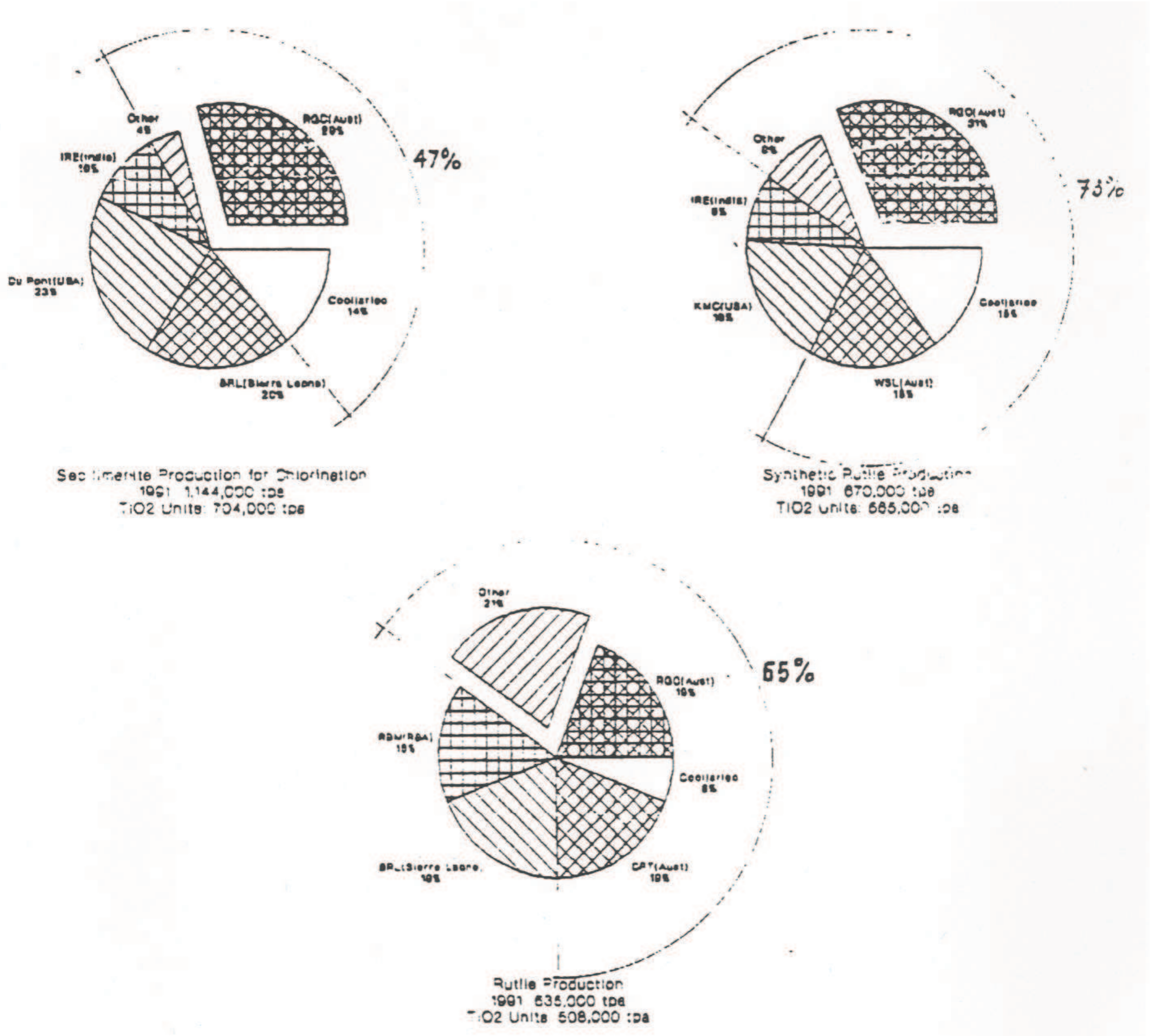


Figure 7. Feedstock Suppliers To Sulphate Process Pigment Plants

### 4.3 Increasing Australian Production

In 1990 when Cooljarloo production reaches the market and Australian production will account for 68% of secondary ilmenite production, 67% of synthetic rutile production and 67% of natural rutile production. (These figures are nett production figures, i.e. ilmenite production of 440,000 tpa from Cooljarloo is adjusted down by 210,000 tonnes used in synthetic rutile production feedstock).



Sec Ilmenite Production for Chlorination
1991 1,144,000 tpa
TiO2 Units: 704,000 tpa

Synthetic Rutile Production
1991 670,000 tpa
TiO2 Units: 665,000 tpa

Rutile Production
1991 635,000 tpa
TiO2 Units 508,000 tpa

Figure 8. World Production 1991

This dominance in output highlights Australia's pivotal role in future supply to both the pigment industry and the titanium metal market.

## 5.0 THE COOLJARLOO INTEGRATED PROJECT

The typical extraction and beneficiation path for titaniferous feedstocks is illustrated by the integrated Cooljarloo project. (The total project concept is shown in Figure 9).

### 5.1 Cooljarloo Mine And Wet Concentrator

The Cooljarloo Orebody is located 25 kilometres inland from the present coastline and 170 kilometres north of Perth, the capital city of Western Australia.

Proven and probably reserves of 569 million tonnes with an average grade of 3.2% and total content of 18.3 million tonnes of heavy minerals put Cooljarloo in the major deposit class.

The typical heavy mineral assemblage is 60% ilmenite, 4.4% rutile, 9.1% leucoxene, 11.2% zircon and 0.6% monazite. Titanium dioxide contents of the titaniferous feedstock minerals are on average, ilmenite 62%, rutile 96% and leucoxene 25%, although the latter fraction encompasses a very broad range.

Mining is achieved with a low unit cost, bulk tonnage floating dredge operation. The bucket wheel suction dredge supplies sand to a feed preparation system of trommels to remove oversize material and hydrocyclones to remove light weight clay rich slimes. From feed preparation, the sand slurry is fed into a spiral concentrator which relies on differential specific gravities to separate valuable heavy minerals from the silicate gangue.

Treatment is via a three stage series of spirals which produce increasing concentration of heavy minerals with each stage up to approximately 92% heavy minerals in the final dewatered concentrate. The sand and slimes tailings from the concentrator are returned to the dredge pond for disposal. Any material with an SG less than 3 is separated in the cyclones and spirals then returned to the mine as waste.

### 5.2 Dry Separation Plant

In preparation for dry separation processing, surface contaminants are removed from the heavy mineral grains by several stages of attritioning.

The clean, dry, heavy mineral concentrate is selectively sorted into conductors, (ilmenite, rutile and leucoxene) and non-conductors, (zircon and monazite) by high tension electrostatic separators.

Differing magnetic properties are used to split the conductive minerals into individual constituents. The non-conductors are processed through magnetic and wet gravity separations to produce zircon, a monazite concentrate and a non-valuable heavy mineral fraction.

Crossbelt magnetic separators are used to separate materials of greatly different magnetic susceptability and induced roll magnetic separators are applied for more subtle differentiation.

### 5.3 Synthetic Rutile Plant

The high $TiO_2$ content feedstocks, rutile and some grades of leucoxene, are fuel for the chloride process pigment plants. Relatively minor sources of ilmenite are suitable for direct chlorination although ore grade ilmenite deposits are in abundance compared with sources of natural rutile.

Ilmenite can be utilised in the chloride pigment process by first upgrading it to synthetic rutile. For Cooljarloo ilmenite, the Improved Becher Process achieves an increase in $TiO_2$ content from 62% to 92% by transforming it to synthetic rutile through the removal of iron and manganese oxides.

The Becher process reduces iron and manganese oxides ti metallic or a sulphidised form in a sulphurous atmosphere, high temperature, coal-fuelled rotary kiln. The process also produces partial reduction of $TiO_2$ to $Ti_2O_3$ and creates a porous crystal structure in the reduced ilmenite.

The iron manganese sulphide is leached from the ilmenite grains with weak sulphuric acid.

Dissolution of the metallic iron phase takes place in an aerated, aqueous bath using an ammonium chloride catalyst. The metallic iron diffuses through the porous network of the ilmenite to the grain surface where it is oxidized to insoluble $Fe_2O_3$. The remnant grain with the iron and manganese salts removed is synthetic rutile with approximately 90-94% $TiO_2$ content.

Precipitated iron oxide is separated from synthetic rutile in hydrocyclones. The product is subjected to a final leaching in weak sulphuric acid to remove manganese and any residual metallic iron before washing and drying to a saleable form.

### 5.4 Chloride Process Pigment Production

Rutile, high grade leucoxene, synthetic rutile and high grade titania slag are suitable feeds for chloride process pigment plants. In the output of waste material, the chloride process is much more environmentally acceptable to the alternative sulphate process.

In the Cooljarloo example, synthetic rutile is reacted at high temperature with petroleum coke and chlorine gas in a fluid bed chlorinator. The reaction produces metal chlorides and other gas. Titanium tetrachloride ($TiCl_4$) is separated from the gas stream and condensed to a liquid which is distilled to remove impurities.

Pure titanium tetrachloride can be used to produce titanium dioxide pigment or titanium metal products.

The oxidation process burns oxygen and pure $TiCl_4$, activated by an aluminium chloride catalyst, to produce $TiO_2$ particles and chlorine gas. The solids and gases are separated before the plant is further treated to enhance its opacifying qualities and the gas is recycled.

Titanium metal can be produced using the Hunter, Kroll or Electrolytic Ginatta processes. The Hunter and Kroll processes react $TiCl_4$ with sodium and magnesium respectively to produce titanium metal and chlorides. The Electrolytic Ginatta process involves electrolysis of $TiCl_4$ to produce metal and chlorine gas.

## CONCLUSION

Many titaniferous metal deposits have been located around the world, however, there are two major constraints for further development:

1. The grade of the deposits are dropping from 9% to 12% mined 10 years ago to as low as 3% to 5%.

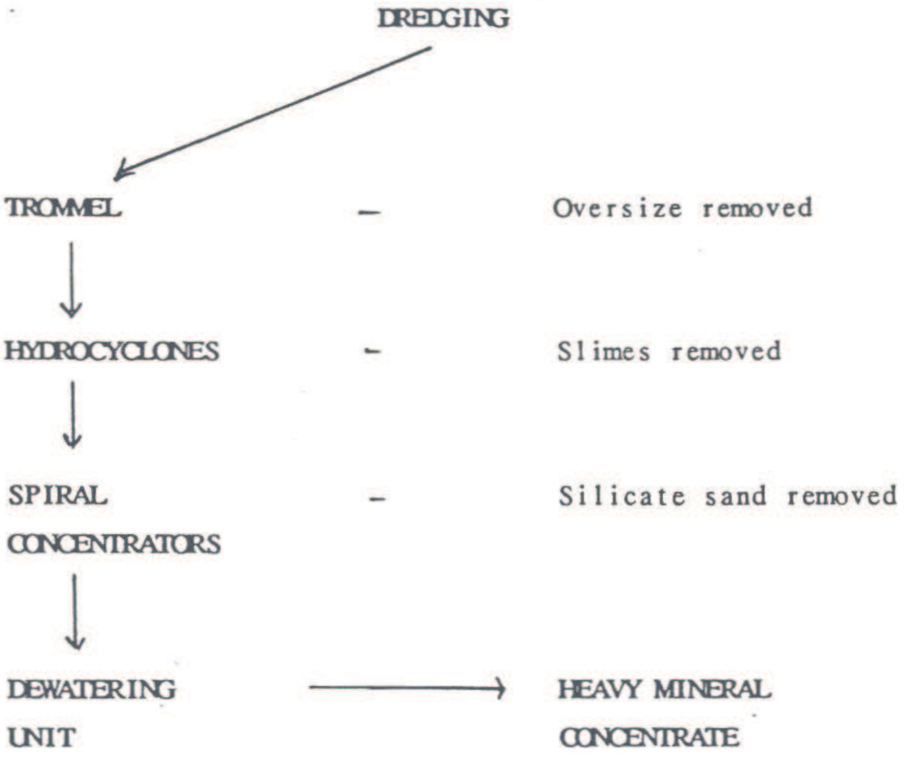
   The lower grade mines need to be extracted using highly mechanised dredging methods which are capital intensive and will require an abundance of water for ponds and processing.

2. Environmental constraints are the biggest factor against new developments because most deposits are near coastlines with more delicate ecological balances and near centres of population.

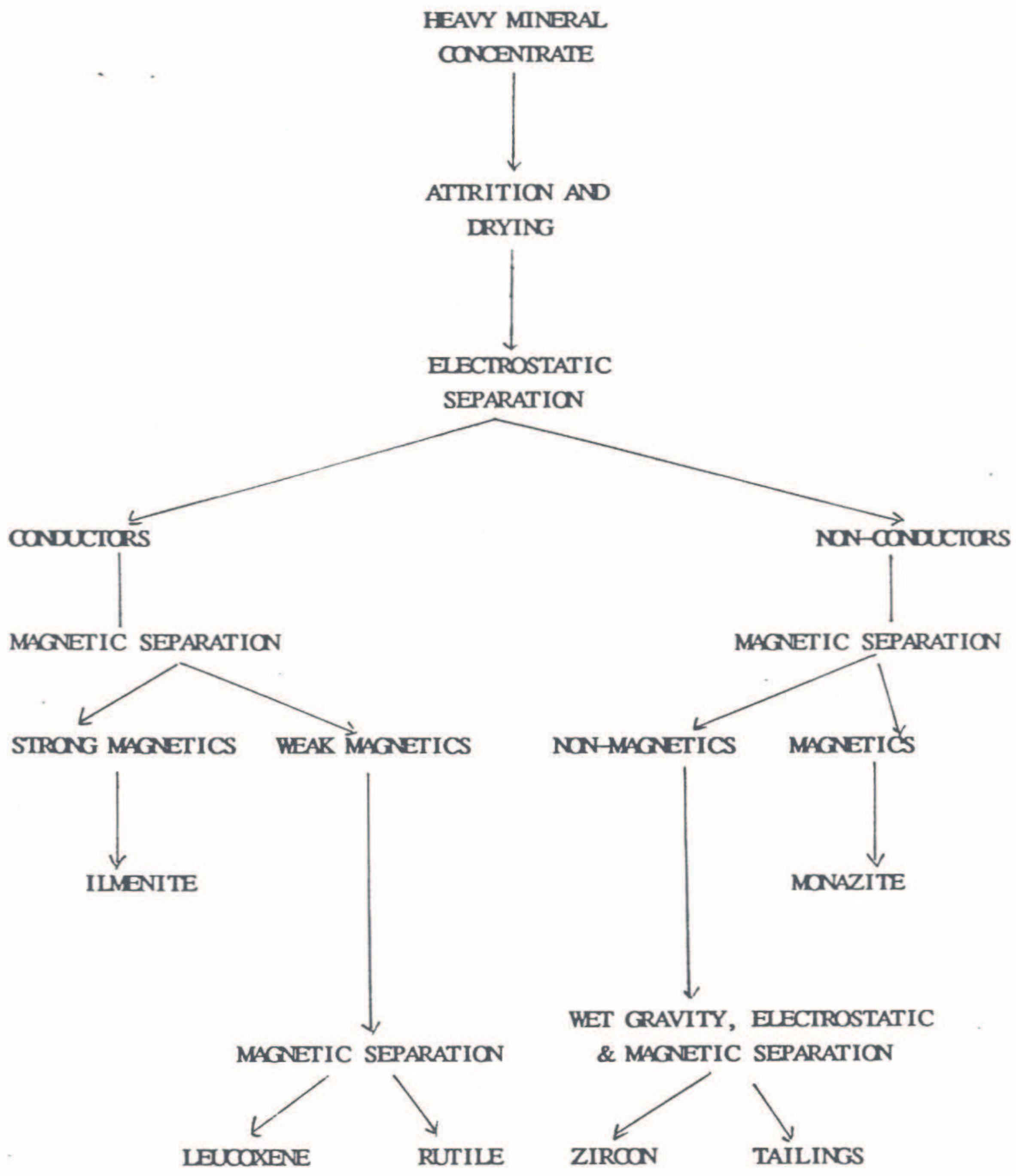
   The mines with lower grades need to strip vegetation over larger areas. However, with proper rehabilitation techniques the land can be readily returned for agricultural use in better condition than the usual mineral and nutrient deficient soil found prior to mining.

Over the next 20 years there are sufficient known titaniferous mineral deposits to keep supplying the world's needs. Any rapid growth in titanium metal production is unlikely to be restricted by production of titanium tetrachloride or titaniferous minerals.

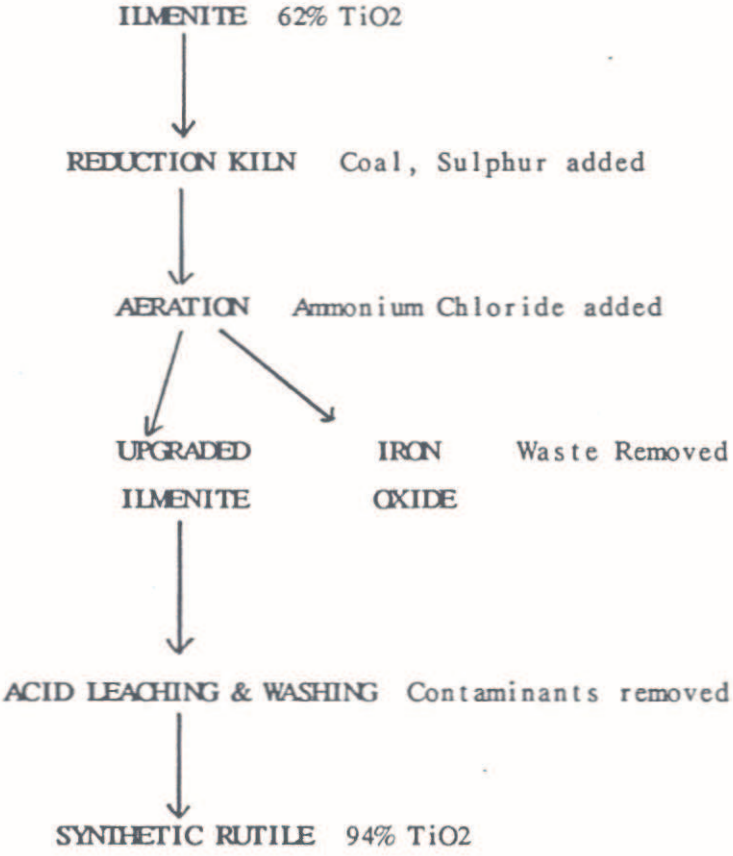
# COOLJARLOO MINE AND WET CONCENTRATION



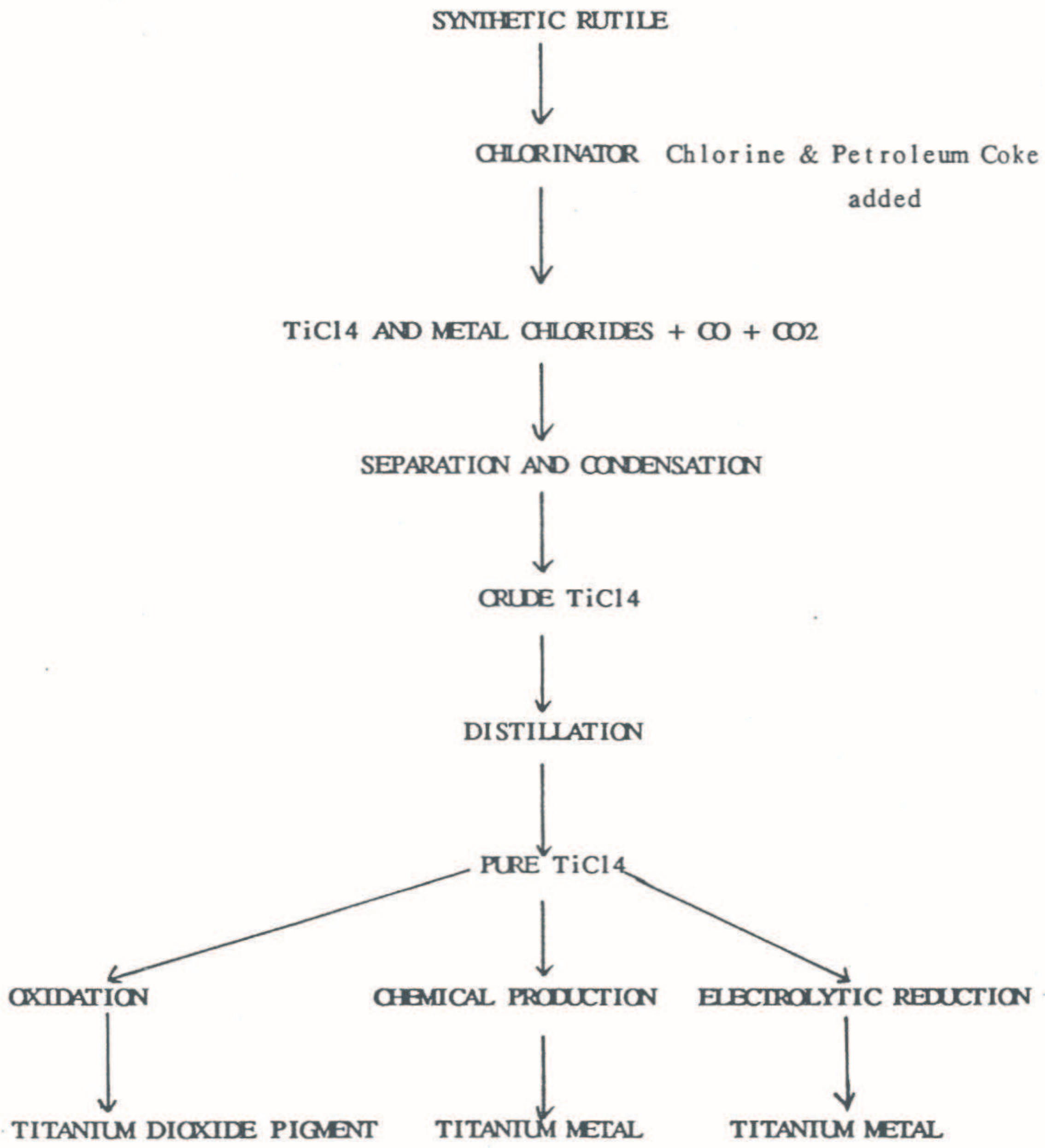
## DRY SEPARATION/CONCENTRATION



## SYNTHETIC RUTILE - IMPROVED BECHER PROCESS



# CHLORIDE PROCESS TiCl4 PRODUCTION & USE



V Meeting Internazionale
Sul TITANO
Organizzato dalla Ginatta
9 Novembre 1989, Torino, Italy

M. Tsutsui, K. Kitaoka, and H. Itoh, Ph D.
Kobe Steel, Ltd.- Japan

# "NON-AEROSPACE APPLCATION OF TITANIUM IN JAPAN"

## Introduction

Industrial applications of titanium materials have been expanding widely in many areas.

Applications of titanium can be classified into two fields, namely aerospace and non-aerospace. From the outset titanium has been mainly used for aerospace applications in the United States.

In Europe both applications, aerospace and non-aerospace, have grown almost simultaneously. The situations in other countries may be similar to that of Europe.

Conversely in Japan, titanium has been used entirely for non-aerospace applications. Recently, however, Japanese aerospace applications are increasing gradually in accordance with the growth of the aerospace industry. We can expect non-aerospace applications, which are extremely varied, to increase greatly in the future. Titanium is still an expensive metal, but the growth of its overall consumption will entail a reduction of production costs which in turn will naturally brine about a further expansion in consumption.

# TITANIUM - Toward The 3rd Metal

Anticipates to its salient features or high resistance to corrosion and heat, light weight and high strength, titanium is being used more and more in the fields of chemical industry, thermal and nuclear power generation, seawater desalination, building or deep-sea survey submarines, and aerospace. Thus finding expanding applications in aerospace, on land and in the ocean, titanium is attracting much attention as a new basic metal for coming generations.

In this paper, the recent status or typical resulting and newly growing applications in Japan will be described. In addition, the problems that need to be solved to allow further expansion of non-aerospace applications will be discussed.

The trends in consumption of titanium mill products in the USA, Europe and Japan are shown in Fig.1.[1)]

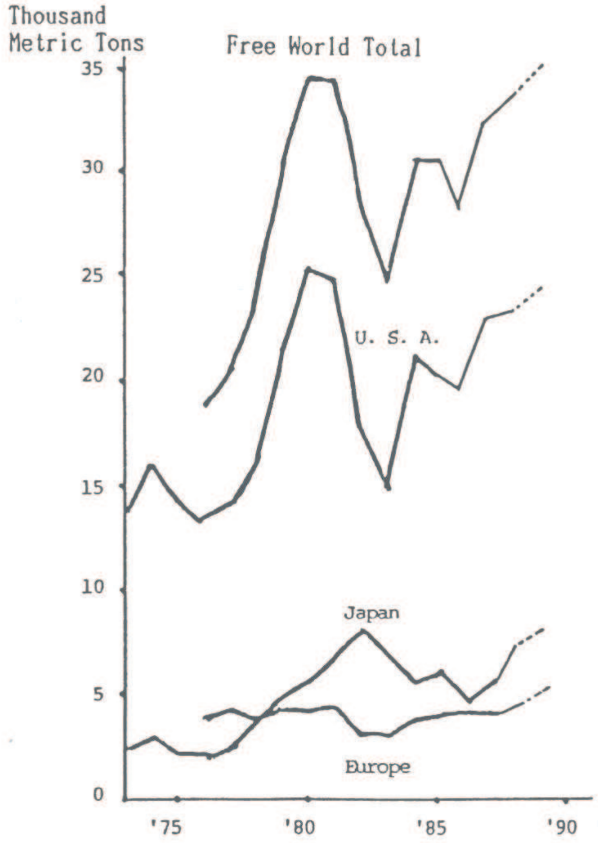


Fig.1 Shipments of titanium mill products in the free world.

## Practical Applications

### 1. Power Plants of Electricities

### (1) All-titan-condenser

Nuclear power plants, PWR- and BWR- types: are of large capacity, term shutdown for protection against radioactive pollution, is an important member of a nuclear power plant and tremendous effort has been made to prevent condenser trouble. The fully titanium tubed condenser was developed with this background, coming into increasing use as the zero-leakage condenser at nuclear power plants around the world as in Japan.

Concerning the strip for seam-welded titanium tubes, development of production technology of large-width, large-sized titanium strip by the use of conventional hot and cold rolling mills has contributed greatly to mass production and cost reduction through high productivity and yield.
Photos 1 and 2 show the reverse cold rolling and annealing/chemical pickling lines, respectively, in the cold-rolling process, after the strip is rolled by a seven-high hot tandem rolling mill.

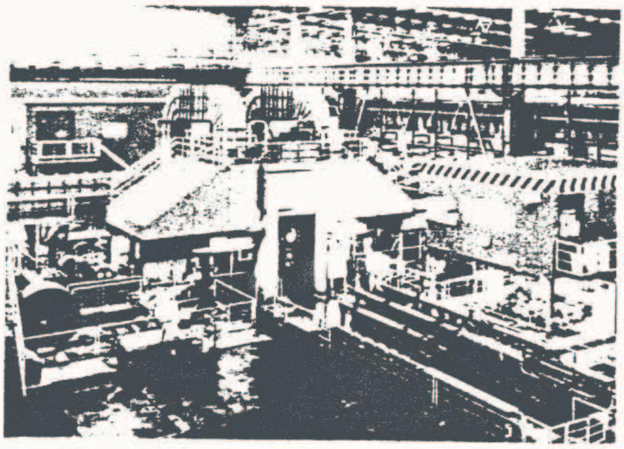


Photo 1 - Reverse cold rolling mill

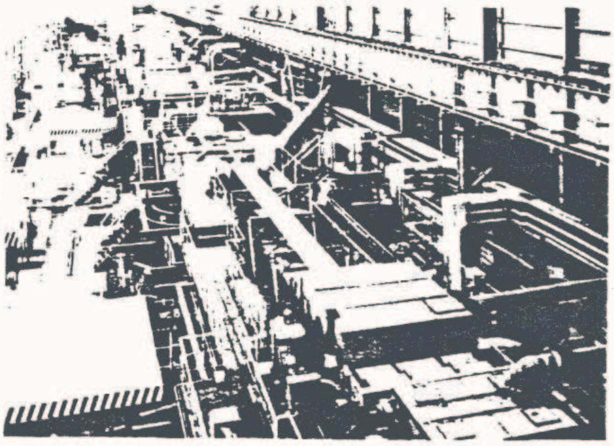


Photo 2 - Annealing and pickling line

To produce welded tubes, it is a common practice to use a tube-forming machine consisting of various tube-forming rolls, as shown in Fig.2, and a non-filler TIG welding machine. Advantages of this production method include high productivity realized by increased tube-forming speed. and excellent welded bead shape and as-welded quality. Applying the high-frequency pulsed arc to the conventional direct-current TIG welding power supply increases arc pressure, maintaining high penetration capacity and stiffness of the arc even in high-speed tube forming, and achieving a smoother bead surface, as may be observed in Fig.3.

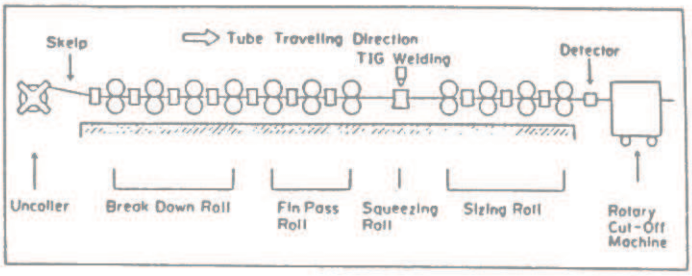
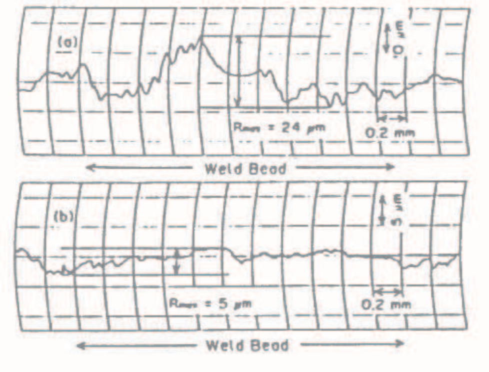


Fig.2  Schematic diagram of tube making equipment



Power source : (a) Conventional DC
(b) High frequency pulsed
Tube size : 25.4 Ø x 0.5 tmm
Welding speed : 5 m/min

Fig.3  Surface roughness measurement for titanium tube weld

Titanium tubesheet stock is precisely machined by a multiple-spindle drilling machine with the NC tape prepared by an automatic design program. Titanium has high resistance to deformation and low thermal conductivity. Therefore, molybdenum-cobalt-based high speed steel is used for cutting drills, and cutting speed is kept of one half that for naval brass tubesheets.

Titanium-clad steel plates (JIS G 3603) are also used for tubesheets for titanium-tubed condensers. In titanium-tubed condensers the tube ends are not machined to have a bell mouth and the tube-hole wall is not grooved.

All-titan-condensers in service stand of 12 units, the total turbine output 12,602 MWe, in domestic nuclear plants as of June 1989, and the units employed titan condenser under construction stand at 13 stations with a total output of 10,407 MWe.

All the units are operating satisfactorily and, all-titan-condensers are enjoying more general acceptance and a growing reputation.2)

Recently, Kakogawa Works No.6 steam turbine of Kobe Steel employed a totally titanium-tubed condenser using more thinner wall 0.4mm thick tubes and titanium-claded steel tubesheet. For ancillary equipments, filters on the seawater inlet side, automatic tube reverse-washing system, and automatic condenser-tube cleaning device using sponge-rubber are introduced. In years to come, the operation performance of the condenser will be reported.3)

### (2) Development of titanium-alloy long blading

Since 1974 Kobe Steel has been carrying out operating tests of 23" long Ti-6Al-4V alloy blades installed in its own 50 MW steam turbine power station at Kakogawa Steel Plant. As shown in Photo. 3, two groups of each five titanium alloy blades are fixed symmetrically keeping the weight balanced.

Beta titanium alloy is overlaid on the leading blades of the titanium alloy blade group for erosion shielding.

The titanium alloy blade with Beta-titanium alloy overlay shows much less erosion compared to 12% Cr Steel blade brazed with Stellite.

This results confirms the effect of Beta-titanium alloy overlay.4)

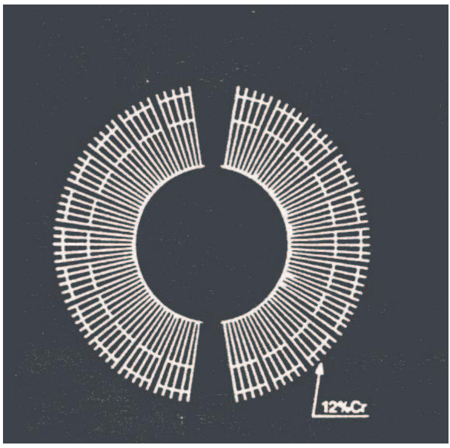


Photo 3
Location of 23" long
titanium alloy blades.4)

At present The Chubu Electric Power pioneerly worked cooperatively with three domestic turbine manufacturers (Toshiba, Hitachi, and Mitsubishi Heavy Ind.) and developed the world-longest 40-inch titanium alloy blade to be mounted on the 3,600 rpm turbines. Table 1 compares the physical properties of "Ti-6Al-4V" alloy with those of conventional high-chromium steel.

Because titanium has insufficient forgeability and anxiously embrittles by absorbing hydrogen or oxygen according to environmental conditions, actual blades were trial-made, and tested to ascertain effects of manufacturing method and process on material properties. The tests proved the "Ti-6Al-4V" can be satisfactorily used for blade material. Photo. 4 shows an example of blades made on trial.

Table 1 Comparison of Physical Properties of
Ti-6Al-4V and High-Cr Steel5)

| Items | Ti-6Al-4V | High-Cr Steel |
|---|---|---|
| Young's modulus | 11,550 kgf/mm² | 22,100 kgf/mm² |
| Poisson's ratio | 0.32 | 0.26 |
| Specific gravity | 4.42 | 7.70 |
| Tensile strength | ≧91.4 kgf/mm² | ≧ 113 kgf/mm² |
| Yield strength (0.2%) | ≧84.4 kgf/mm² | ≧ 78 kgf/mm² |
| Elongation | ≧10% | ≧13% |
| Reduction of Area | ≧25% | ≧30% |

In the supersonic area, blades-cascade loss increases due to shock wave. To accommodate such loss, blade performance was investigated and the basic specifications were determined as shown in Table 2.

Table 2 Basic Specification of L.P. Last Stage Blades5)

| Items | Long titanium alloy-blades | 700 MW's conventionals |
|---|---|---|
| Length | 40" (1,016 mm) | 33.5" |
| P C D | 104" ～ 107.2" | 90.5" |
| Annular area | approx. 8.5 ㎡ | 6.1 ㎡ |
| Circumf'l speed at blade-tip. | approx. 700m／sec. | approx. 600m／sec. |
| Numbers | 68 ～ 90 pcs. | 94 pcs. |
| Type of root | Contrary-Christmas tree or Fork type | Fork type |
| Material | Ti-6Al-4V | 12Cr steel |
| Weight | 16 ～ 23 kg／pcs. | 16.7 kg／pcs. |

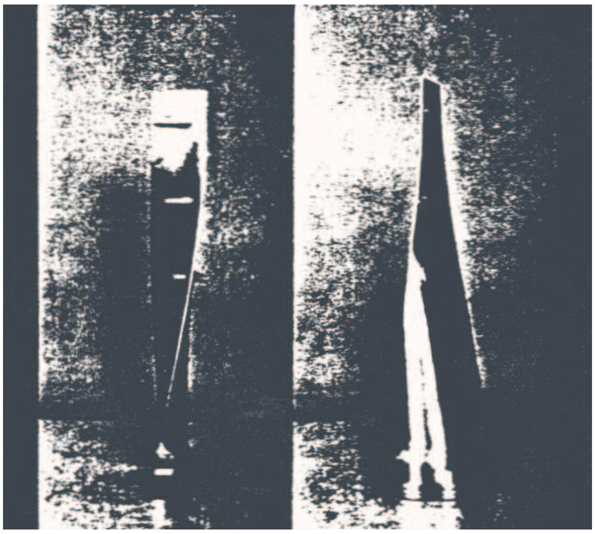


Photo 4 3,600 rpm 40-inch
Ti-6Al-4V blade4)

Fig. 4 shows that better thermal efficiency of 1.5% or a saving of several million US$ annually by using 40" long titanium alloy blades, which are now under development, will be achieved, compared to the conventional Hi-Cr Steel blades, when actually applied to a 700 MW commercial steam turbine.

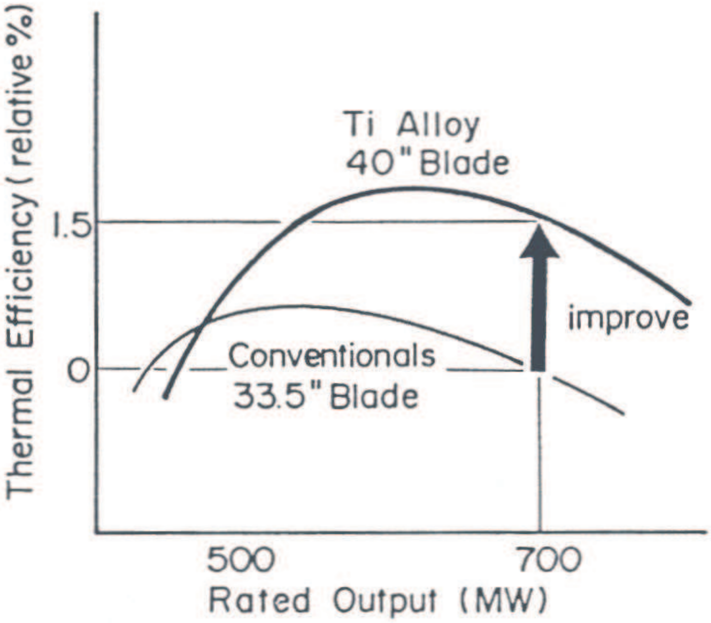


Fig. 4
Improvement of thermal efficiency applying of 40" long titanium alloy blade.[5)]
Courtesy of Chubu Electric Power Co.

At present concrete investigation has been made on the application of long blades to the steam turbines No. 1 to 3 of The Hekinan Thermal Power Plant of The Chubu Electric Power now just under construction.5)

(3) Spent nuclear fuel reprocessing

In the spent nuclear fuel reprocessing by Purex process using nitric acid ($HNO_3$), stainless steels have been used for the process equipment although some leakage, caused by the corrosion of the material, has been experienced.

Therefore, it is expected that new type materials which have better corrosion resistance against $HNO_3$ solutions are developed.

As is known well, Zirconium (Zr) , Titanium-5% Tantalum alloy (Ti-5Ta) and Titanium (Ti) have an excellent corrosion resistance against $HNO_3$ solutions and so they seem to be appropriate materials for the Purex process equipment.

However, their corrosion resistance in the Purex process environment has not yet been clearly demonstrated.

Thus, the corrosion behaviors of Zr, Ti-5Ta and Ti were studied in simulated reprocessing environments (non-radioactive) , that is in $HNO_3$ solutions with and without the fission product elements Ru, Rh and Pd ions.

As shown in Fig. 5, Ti-5Ta alloy shows superior corrosion resistance in a concentrated boiling nitric acid solution compared to normal CP grade. The main feature of this alloy is that it is entirely free from SCC problems. Moreover, it is easier to fabricate than zirconium. Therefore, Ti-5Ta alloy is now seen as the most promising future material for nuclear fuel reprocessing application.$^{6)}$

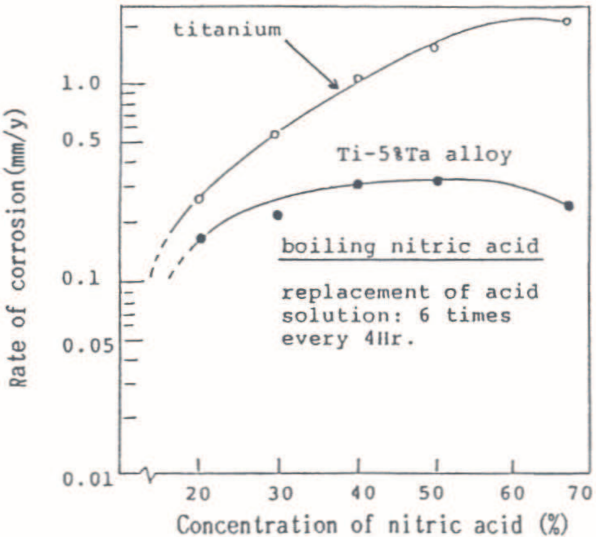


Fig.5 Rate of corrosion of Ti and Ti-5%Ta alloy in nitric acid

(4) Nuclear waste management program (Canister)

The reprocessing of spent nuclear leaves behind high-level radioactive waste which must be stored securely.

At present, spent nuclear fuel and high-level waste are temporally stored in indors, and stored in underground tunnels after a certain period of indoor storage is under consideration.

In this case, the waste would be put into metal canisters with an additional over-pack. However, due to the heat emission, the metal of such packing is expected to suffer from crevice corrosion.

ASTM Grade 12 (Ti-0.8Ni-0.3Mo, G12), which is resistant to high temperatures and crevice corrosion, is considered to be one of the candidate materials for such over-packing although there are a number of problems to be solved before making a decision on the underground storage of radioactive waste.

Wide coils, thick plates, and thin-wall seam-welded tubes produced from a large-scale ingot of G12 were investigated as to corrosion resistance, mechanical properties, weldability and so on. It was clarified that the G12 alloy has several advantageous features: the crevice corrosion resistance of the alloy was almost equal to those of G7 and PdO/$TiO_2$-coated Ti, and the maximum allowable stress was able to be designed higher than that of C.P.Ti. It is expected that industrial applications of the G12 alloy will increase owing to its low cost and high durability.

G12 wide coils and thin-wall welded tubes were manufactured on a commercial production basis, and corrosion resistance, physical properties, and weldability were investigated. It was confirmed that G12 provides far superior corrosion resistance, especially crevice corrosion resistance as shown in Fig.6, to C.P.Ti and has properties close to G7 and PdO/$TiO_2$-coated Ti. From the viewpoint of cost, G12 is less expensive than G7 or PdO/$TiO_2$-coated Ti.

In years to come, it is expected that G12 will replace C.P.Ti for prolongation of lite or to cut down the cost of G7 and PdO/$TiO_2$-coated Ti, and that the demand for G12 will increase.7), 8)

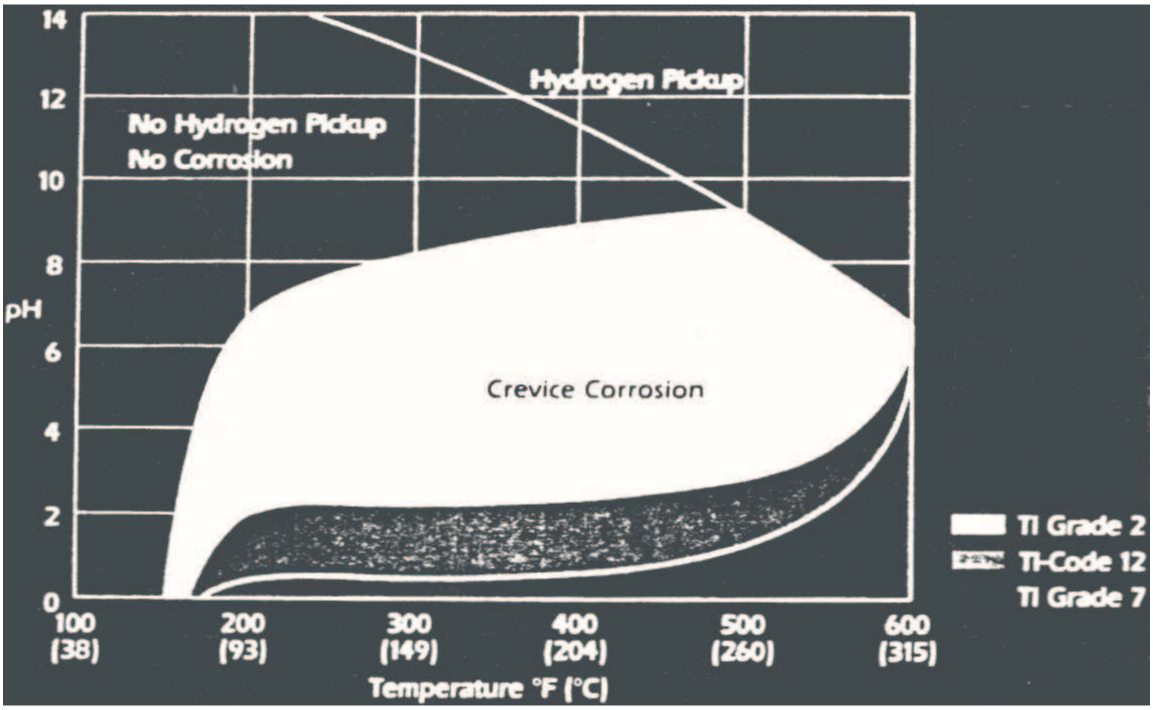


Fig.6 Crevice corrosion properties of Titanium Grades 2, 7 and 12 in saturated NaCl brine.7)

(5) Robota

Japan Atomic Energy Research Institute (JAERI) developed a prototype light-duty underwater manipulating Robot, as shown in Photo 5. of 10kg/100kg loading capacity employing Ti-6Al-4V made gear as form a part of JPDR reactor decommissioning technology.

The manipulator has high performance of seven freedoms of movement and seven hinges.

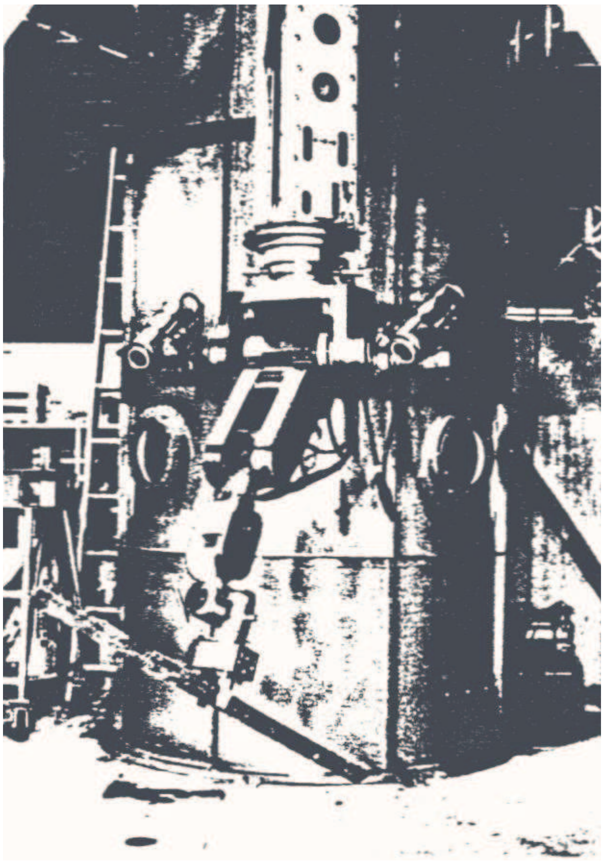


Photo 5 Outside view of Prototype light-duty underwater manipulator. Courtesy of JAERI and Mitsubishi H.I.

## 2. Automotive Parts

In 1989. Yamaha (Japan) adopted a surface-nitrided Ti-6Al-4V connecting-rod for a limited model of motorcycles (Photo 6). The parts have the most potential in automobile production model. The development of a low-cost, durable surface treatment and assurance of the material's durability are essential in order to use titanium and its alloy in automotive parts (Photo 7).

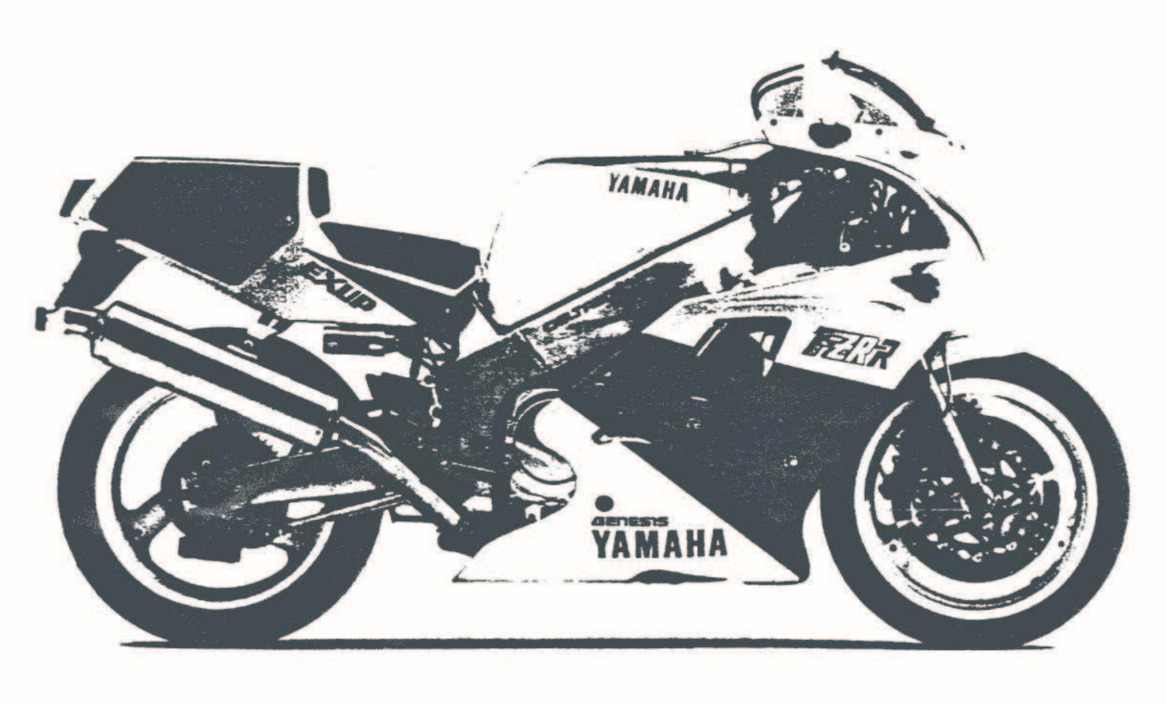


Photo 6 Yamaha FZR750-R Motorcycle
Courtesy of Yamaha Motor Co.

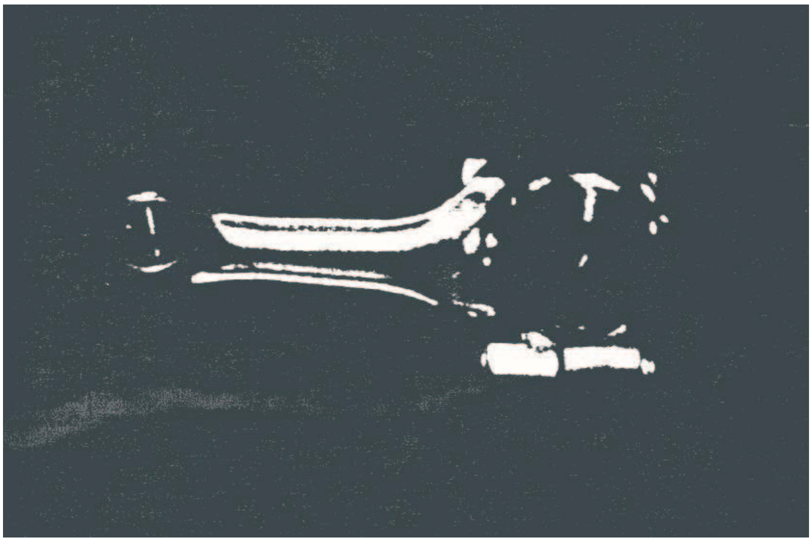


Photo 7 Ti-6Al-4V Connecting rod
ibid.

## 3. Personnel Pressure Hull for Deep-Sea Submersible

The first Japanese deep sea submersible of 2,000 m depth capability, named as "Shinkai 2000" was completed in 1981.

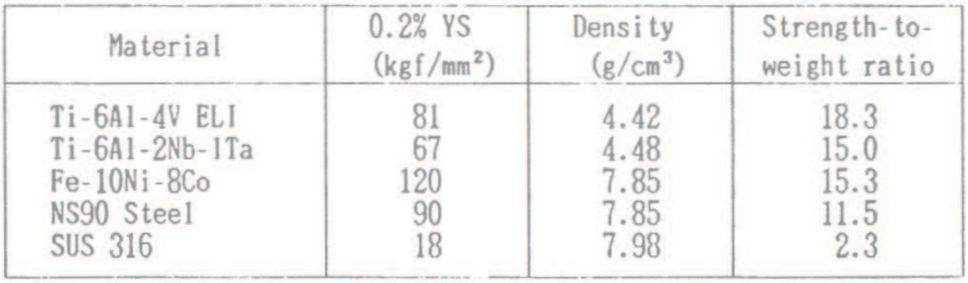
Continuously, Japan has constructed a deeper sea research submersible operating at or more than 6,000 m depth.

Research on technology to manufacture a titanium alloy pressure hull applicable to this submersible has been conducted by Mitsubishi Heavy Industries and assist with Kobe Steel.

Ti-6Al-4V ELI has been chosen for a pressure hull material because of the high strength-to-weight ratio, as shown in Table 3.

Ti-6Al-4V ELI 9-ton ingot was forged and rolled down to 110 mm thick plate to take a blank. The large plate was hot formed using a 13,000 ton press to make a hemisphere of 2,000 mm diameter. The primarily machined hemisphere was welded together with view ports and penetrator by electron beam welding method. Hemispheres could be electron beam welded together to sphere only for 18 minutes. Photo 8 shows a article "Shinkai 6500" having the 73.5 mm thick titanium alloy pressure hull.[9)]

Table 3 Strength-to-weight ratio of various materials for submersible pressure hull



| Material | 0.2% YS ($kgf/mm^2$) | Density ($g/cm^3$) | Strength-to-weight ratio |
|---|---|---|---|
| Ti-6Al-4V ELI | 81 | 4.42 | 18.3 |
| Ti-6Al-2Nb-1Ta | 67 | 4.48 | 15.0 |
| Fe-10Ni-8Co | 120 | 7.85 | 15.3 |
| NS90 Steel | 90 | 7.85 | 11.5 |
| SUS 316 | 18 | 7.98 | 2.3 |

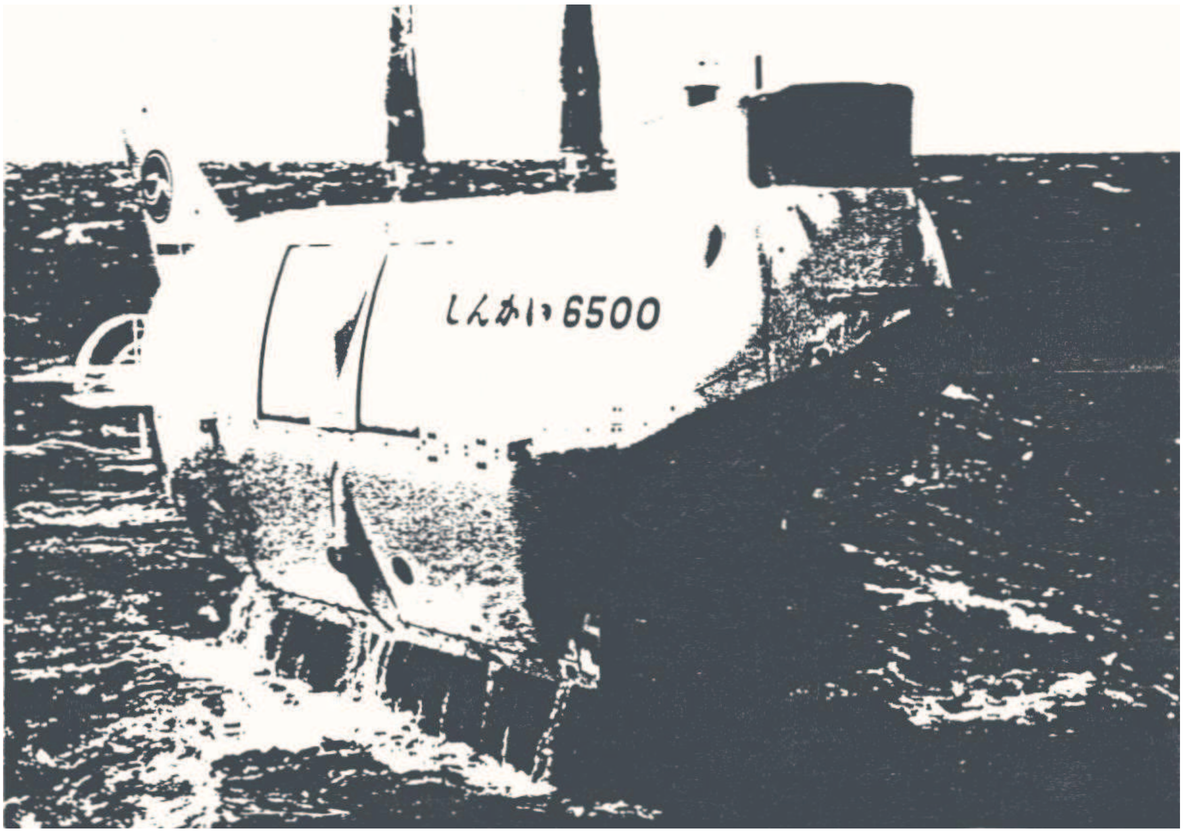


Photo 8 "Shinkai 6500"
Courtesy of Japan Marine Science and Technology Center and Kobe Shipyard & Machinery Works, Mitsubishi Havy Ind., Ltd.

## 4. Architecture and Civil Engineering

In Japan titanium has been used for sometime as a building material such as roofings, domes, curtainwalls, monuments, esteriors, interiors, etc. In 1987, about 12 tons of titanium sheets was used for the roofing of Kobe Municipal Aqua-life Museum as shown in Photo 9 and a magnificient sanctuary which used 90 tons of titanium was also erected.

Although titanium is still costly compared with the conventional high grade materials such as copper, aluminium and stainless steel it is attracting great interest of the people concerned as a new building material for the future not only because of its superior corrosion resistance but also because of its fashionable and artistic image.

Photo 9 Kobe Municipal Aqua-life Museum at Suma with titanium roofing of 2,330 $m^2$ using 12 metric tons of titanium sheets of Kobe Steel.

Effects of various properties, every possible elastic and plastic tensile properties, grain size or impurity compositions on a magnitude of pocket waves were examined carefully. As a result, a magnitude of pocket waves was found to have a significant interrelation particularly with a grain size of original titanium sheet, as shown in Fig.6. It becomes evident that titanium sheets with finer grains (larger grain size number) are more effective in preventing the pocket waves. These specimens had the respective microstructures shown in Fig.7. It is clear that fine grained Specimen B has a superior appearance free from pocket waves compared to coarse grained Specimen A.

Various tests and investigations were made to construct the peculiar titanium roof of Suma Aqualife Park. Developed roll-forming technology and special titanium sheets for construction use were applied to the actual construction and satisfactory results were obtained. The special titanium sheets have given actual results in several other roofs including them of seam welded structure.

In future, the advantages of titanium such as corrosion resistance and easy maintenance will be confirmed. It is convinced that demand for titanium will expand more and more in construction field.10)

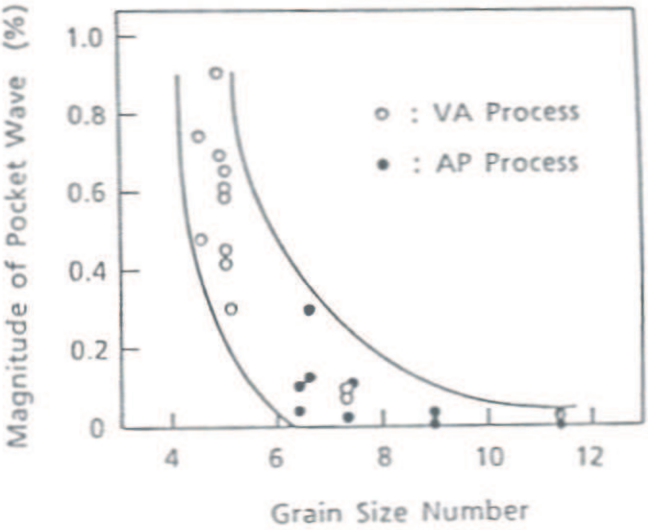
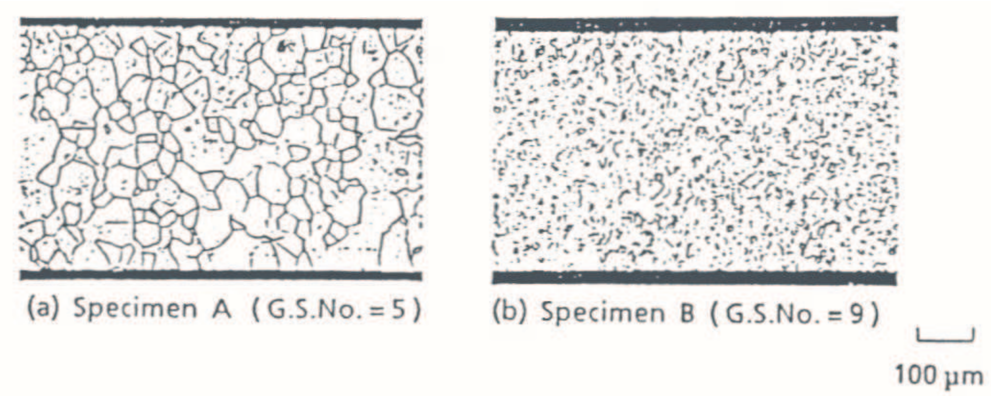


Fig.6 Relation between the magnitude of pocket waves and grain size number10)


(a) Specimen A (G.S.No. = 5)

(b) Specimen B (G.S.No. = 9)

Fig.7 Microstructure of formed specimens 10)

# Epilogue

With its outstanding resistances to corrosion by seawater, comparable to that of platinum, titanium is also a "metal for the sea".

The field of ocean development, in which many of man's dreams for the future are being realized, encompasses an expanding variety of uses for titanium, such as equipment and components for ships, including deep-sea submergible vehicles, and equipments required for seabed resources, oil wells on continental sheives, off-shore fish farms, bridges across the sea, artificial islands, and cities on the sea.

In addition to these uses, titanium is also used for its beauty and other special features in the manufacture of articles of daily necessity, including eyeglass frames, cameras, writing instruments, cigarette lighters, jewelry, and a variety of sports goods, such as tennis and badminton racket frames, golf club shafts, bicycles, motorcycles, yachts and mountain-climbing equipment.

Because of its bioacceptability, titanium is also attracting attention as a material for the manufacture of articles for medical purposes, such as artificial bones, artificial dental implants and heart pacemakers, thus indicating that the metal is bound to become an indispensable material as the elderly population continues to increase.

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Alessandro Manfredi, Comepre s.r.l.

# LA SALDATURA DEL TITANIO IN CABINA PRESSURIZZATA

Signore e Signori, Buon Giorno.

Prima di tutto mi sento in dovere di ringraziare la Società Ginatta Torno Titanium ed i suoi collaboratori per l'invito fattomi per questo 5° meeting sul titanio.

L'argomento che tratterò riguarda la saldatura del titanio, in particolar modo in cabina pressurizzata metodo T.I.G.

Di tale sistema sono ritenuto un esperto in quanto ho avuto la fortuna di progettare e costruire la prima cabina nel lontano 1962: questa cabina è tuttora funzionante dopo oltre 25 anni di lavoro, aggiornamenti e collaudi continui in Comepre, e Vi dirò con risultati veramente eccezionali.

Il titanio è un metallo nobile che fonde alla temperatura di circa 1589° e che purtroppo a circa 400° inizia la sua variazione di struttura, che da alfa passa in beta, per l'assorbimento di idrogeno e ossigeno dell'aria, divenendo cristallino quindi molto fragile: per ovviare a questo, ecco la cabina la quale altro non è che un serbatoio abbastanza grande dove viene fatto un vuoto relativo di 10 -3 e ristabilizzata mediante Argon.

La difficoltà maggiore è quella di ottenere internamente una temperatura costante da 45 a 55° e un'umidità relativa di quasi 0%. Detto questo a grandi linee passiamo alla preparazione dei pezzi.

La preparazione dei pezzi per la saldatura deve essere molto accurata: prima di ogni cosa le superfici da saldare non devono assolutamente essere molate, in quanto il carborundum della mola viene assorbito dal titanio, al che in fase di saldatura queste particelle di carborundum galleggiano nel bagno quindi creano poi problemi in radiografia.

Quindi per l'asportazione è consigliabile l'uso di utensili metallici.

Fatto questo i particolari devono essere lavati con acetone; intendiamo bene, acetone puro e non il famoso MET di cui tanto si parla che non è altro che una soluzione di metilchetilcetone, petrolio ed altri componenti che non Vi sto ad elencare, i quali oltretutto sono anche nocivi.

Fatto tutto questo si dispongono i pezzi nella cabina: non si devono toccare i pezzi a mani nude perché il tatto umano cioè il sudore altera le zone da saldare.

Voglio subito dire che la saldatura in cabina pressurizzata dà la costante durezza diciamo di un titanio Gr. 1 cioè una durezza media di 180 HB con un possibile aumento della stessa da 2 a 4 punti beninteso se vengono usati i sistemi di preparazione sopra detti, quando per saldatura effettuata all'aria, cioè non in cabina pressurizzata, i punti variano di circa 20-30 semprechè si usino dei sistemi di protezione Validi.

Inoltre in cabina pressurizzata, la velocità di saldatura è di circa 5/6 metri ora, mentre all'aria circa 1 metro ora.

Da prove fatte in Comepre su saldature con filo di titanio, a questo punto non me ne vogliano gli amici venditori, si è potuto notare che era tutto perfetto solo che in fase di radiografia si riscontrano puntini neri che vengono poi qualificati inclusioni di gas.

Siamo giunti a scoprire che usando striscioline di lamiera dello stesso materiale questi punti non compaiono più, al che siamo andati a fondo della cosa, non meravigliateVi di questo perché in COMEPRE si effettuano settimanalmente provini i quali sono sottoposti a tutte le prove sia macrografiche che radiografiche perché è una politica della società di avere sempre gli impianti in perfetta regola.

Dicevamo dei punti neri, non è inclusione di gas ma bensì sporcizia.

Ora devo spezzare una lancia a favore dei famosi colori della saldatura.

I vari rossi... blu... verde ecc. che si dice che è una saldatura anomala, non è vero niente; i colori vengono se non si effettua la pulizia dei pezzi o non la si cura abbastanza: i vari colori dipendono soprattutto dalle impurità e dalla temperatura del bagno.

Infatti spazzolando il pezzo diciamo colorato si nota solo una leggerissima patina superficiale se si tratta di spessori da 0.5-1 a 5-6 mm (cioè non avvengano colorazioni), mentre se si passa a spessori oltre, la colorazione si nota: questo avviene appunto per l'accumulo della massa quindi aumento di temperatura e un notevole tempo di raffreddamento.

La cabina pressurizzata Vi consente di saldare con il tungsteno della torcia molto sporgente, sino a circa 120 mm, permettendo così di effettuare saldature che altrimenti solo con elettrodi sarebbero possibili.

Dopo averVi dato tutta questa infarinatura del procedimento, Vi posso garantire che le società in possesso di dette cabine possono effettuare operazioni uguali su tutti i metalli con risultati veramente eccezionali.

Con questo mio intervento Vi ringrazio tutti per avermi pazientemente ascoltato e qualora ci fossero al riguardo domande eccomi qui.

GRAZIE

# HYDROGEN UPTAKE RATES FOR GRADE 12 TITANIUM IN HOT ALKALINE BRINE MEDIA

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## INTRODUCTION

Applications of grade 12 titanium in concentrated brine media are numerous and diverse throughout the CPI.[1] Many of these applications are due to the extended regime of corrosion resistance offered by grade 12 titanium, as compared with unalloyed titanium.[2] In particular, the excellent crevice corrosion resistance of grade 12 titanium has made it very attractive to salt producers. Salt crystallizers, with near saturated brine feed material, and temperatures over 105°C, have experienced crevice corrosion failures of unalloyed titanium. Grade 12 titanium, however, is resistant to crevice attack in these near neutral (pH 5-8) brine solutions to temperatures in excess of 250°C[3], and has provided years of trouble-free service in this application.

A recent application of grade 12 titanium tubing involved use in a triple-effect evaporator, producing salt from a concentrated natural brine. A pretreatment process on the brine raised the alkalinity of the brine to around pH 12. Due to the high pH and temperatures (about 115°C) involved, concerns were raised about possible hydrogen embrittlement of the titanium. Although published pH-temperature guidelines exist for alkaline hydrogen uptake[2,4], they were developed on unalloyed titanium. The addition of nickel as an alloying agent in grade 12 titanium raises concerns for increased hydrogen uptake in alkaline solutions.[5] The addition of nickel stabilizes beta phase in titanium, which is known to be more susceptible to hydrogen uptake.[6] Also, the guidelines were developed in pure NaCl; the effect of salt mixtures had not been determined.

The intent of this work was to generate guidelines specific to grade 12 titanium for avoiding deleterious hydrogen uptake in caustic brine media. Several factors were assessed as to their effect on hydrogen uptake. These included brine pH, temperature, and composition, as well as alloy surface condition and exposure time. A predictive model was also developed to offer some insight into long-term hydrogen uptake on grade 12 titanium exposed to hot alkaline brine solutions.

# EXPERIMENTAL

ASTM grade 12 titanium (Ti-0.3Mo-0.8Ni) mill-produced strip material was utilized for this study. Analyzed composition of the material (0.29% Mo, 0.73% Ni, 0.13% O, 0.12% Fe) fell well within ASTM specifications. All exposure test coupons extracted from the 0.89mm gage sheet material, were 51mm x 19mm. Analyzed base level hydrogen content of the sheet material was 39 ppm. Prior to exposure, all samples were immersed in an ambient temperature 35 vol. % $HNO_3$/5 vol. % HF solution for approximately 5 minutes. The samples were then rinsed in distilled water and air dried. This procedure constituted the "as-pickled" surface condition. The "thermally oxidized" surface condition involved subsequent air annealing at 650°C ± 10°C for 5 minutes, air-cooled.

Two brine compositions were tested; saturated NaCl, and a simulated natural brine feedstock for a salt evaporator process. The natural brine, as it will be henceforth designated, consisted of 21% NaCl, 5% KCl, and 3.7% $Na_2SO_4$, all by weight. NaOH was used to adjust pH, whose values are reported at 25°C. Balance of all solutions was de-ionized water. All chemicals were of reagent grade purity.

Brine exposure temperatures were 107°C (boiling) and 121°C. The 107°C exposures were carried out in 1 liter test vessels constructed from titanium. This minimized solution contamination, most notably from glass. These caustic solutions tend to etch glass vessels, producing undesirable silaceous deposits on the titanium specimens. These vessels did however utilize glass reflux condensers to prevent solution evaporation. Boiling solutions were refreshed every seven days. The 121°C exposures utilized 2 liter titanium-lined autoclaves. These solutions were refreshed once each month. All test specimens were suspended in test solutions on titanium wire hangers. Each wire was Teflon® tape wrapped to provide electrical isolation between specimens.

Linear polarization studies were performed on an EG&G Princeton Applied Research Model 273 computer controlled potentiostat/galvanostat. Model 342 corrosion software was utilized to conduct the polarization tests. Grade 12 titanium described above was used as the test material, with 1 $cm^2$ surface area exposed to the solutions. All tests were carried out at 107°C. A one liter titanium vessel was used to minimize contaminant interference during testing.

Hydrogen uptake efficiency (HUE) testing, which has been described elsewhere[7] was also performed in the specially constructed titanium vessels described above. Galvanically controlled charging tests were performed with an EG&G Princeton Applied Research Model 273 potentiostat/galvanostat. Current density was varied between 0.05-1.00 $mA/cm^2$, with charging times inversely proportional to current density, so as to maintain a constant hydrogen production rate. All HUE tests were carried out at 107°C.

Post exposure specimen evaluation consisted of bulk hydrogen analysis. Hot vacuum extraction was utilized for hydrogen analysis. Samples were analyzed in duplicate unless results differed by more than 10%, in which case a third analysis was made. In either case, average hydrogen uptake (ΔH) is reported, which is the difference between average post-test hydrogen and the aforementioned base-line hydrogen content.

## RESULTS

Hydrogen uptake results for grade 12 titanium immersion exposures in caustic brine media are shown in Tables 1-3. The data are reported according to brine media, temperature, pH, and surface condition. Tables 1 and 2 represent data from exposures in natural brine at 107°C and 121°C, respectively. Saturated NaCl results are reported in Table 3.

Linear regression plots of selected [ΔH versus exposure time] results were prepared to more clearly see effects of the variables studied (see Figures 1-3). Figure 1 illustrates uptake rates for as-pickled and thermally oxidized grade 12 titanium in pH 12.0 and 12.5 natural brine at 107°C. A small but finite uptake rate appears to occur for pH 12.5 brine exposure specimens in the as-pickled surface condition. The pH 12 as-pickled specimens exhibit a parallel slope to the pH 12.5 specimens, but with a reduced offset. Thermally oxidized specimens exhibit relatively flat hydrogen uptake rates, suggesting little or no time dependence.

Figure 2 reveals, somewhat surprisingly that the 121°C natural brine exposures produced slightly lower hydrogen uptake than the 107°C exposures. The as-pickled specimens appear to exhibit a small positive uptake rate, while thermally oxidized specimens have little or no time dependent uptake rates. Interestingly, as-pickled specimens exposed at pH 13, although not plotted, exhibited significantly higher hydrogen uptake rates as compared to those at 107°C (see Tables 1 and 2).

Figure 3 illustrates the hydrogen uptake characteristics of grade 12 titanium in saturated NaCl at 107°C. From comparing Tables 1 and 3, one can deduce that pure NaCl has a much greater effect on hydrogen uptake than the simulated natural brine. This difference is also exemplified in Figure 3, which illustrates for instance, the very high hydrogen absorption rates for as-pickled specimens in pH 12.5 brine. Thermal oxidation appears to provide much less benefit in saturated NaCl brine. uptake rates for thermally oxidized specimens at pH 12.5, although diminished somewhat from the as-pickled specimen rates, represent unacceptable hydrogen absorption in terms of eventual metal embrittlement.

Hydrogen absorption rates calculated from the linear regression analysis equations of data in Figures 1-3, is presented in Table 4. The values given are for thin wall strip material, 0.89mm gage, and assume that only one side of the titanium is exposed to the hot caustic brine media. This analysis indicates almost a six-fold increase in hydrogen absorption rates for grade 12 specimens in pH 12.5 saturated NaCl, as opposed to the simulated natural brine. For comparison, the actual one year hydrogen uptake results (yearly average based on 52 and 78 week data) are shown as well. The numbers are halved to reflect a single side exposure, so that direct comparison can be made with the regression calculated rates.

Table 5 contains information on the predictive hydrogen uptake model developed using hydrogen uptake efficiency (HUE) testing and corrosion rates determined via linear polarization. The predicted rates were determined on as-pickled grade 12 titanium specimens, in saturated NaCl and the simulated natural brine, at 107°C. Brine pH values of 12.0 and 12.5 were used in developing the model. Since the predictive model yields uptake data for single sided exposures, the actual uptake results were halved for the sake of comparison, as above for the regression analysis comparison.

## DISCUSSION

The mechanism of hydrogen absorption by grade 12 titanium in hot alkaline brine media is based on finite general corrosion attack of the alloy in these high pH solutions. This slow anodic dissolution of the titanium oxide film allows cathodic breakdown of water at the metal surface, generating nascent hydrogen. The nascent hydrogen then reacts to form titanium hydride. At temperatures above 80°C, the hydrogen diffuses into the titanium, causing eventual embrittlement of the metal.

Hydrogen absorption in this study was quite variable, as evidenced by the tabulated uptake results. Since the formation of titanium hydride occurs at the metal surface, compositional variations in the surface film will affect hydrogen absorption. Thus, oxide film growth during high temperature solution exposure, which is known to occur[2], could quite likely be the major cause of uptake variations. It most likely also produces the "leveling off" of hydrogen uptake data observed for many of the conditions plotted in Figures 1-3. As the oxide film increases in thickness, the corrosion rate of titanium is diminished, thus increased exposure times lead to a static level of hydrogen uptake.

Thermal oxidation, which has been shown to be an effective barrier to hydrogen absorption in reducing acid environments[8], appears to have a neutral to positive effect on hydrogen uptake in alkaline media, depending on brine make-up and pH. At pH ≥ 12.5, the thermal oxide serves to diminish the uptake rate somewhat. However, in saturated NaCl, the uptake rate is not reduced sufficiently to eliminate eventual hydrogen embrittlement. This is not the case in the natural brine at pH 12.5, in which thermal oxidation lowered the uptake rate by 50%, putting it into a regime of innoccuous hydrogen absorption. Uptake rates at pH 12 were not significantly affected by thermal oxidation. The most likely explanation being due to the oxide film buildup occurring during solution exposure, negating the effect of any pre-existing thermal oxide film.

Temperature had mixed effects on hydrogen uptake of grade 12 titanium. Increasing temperature lowered uptake rates at pH ≤ 12.5, yet increased the uptake rate at pH 13. The explanation for this is possibly due to more rapid oxide film growth during solution exposure at 121°C when low corrosion rate conditions prevail (pH 12 and 12.5). While at higher corrosion rate, such as pH 13, the corrosion (and subsequent hydrogen absorption) overwhelms the faster oxide film buildup.

Brine composition appears to influence hydrogen uptake only at pH levels above 12.5. At these higher pH levels, saturated NaCl significantly increased hydrogen absorption rates on grade 12 titanium. The cause of the increased uptake rates is due to much higher corrosion rates at pH 12.5, in saturated NaCl. In fact, at pH 12.5, the corrosion rate more than doubles for grade 12 titanium in saturated NaCl, compared with natural brine. However, at pH 12, the corrosion rates were identical.

Linear regression of the hydrogen uptake data was utilized as a conservative approach for data analysis. Generally, good line fits were obtained only on the highest uptake rates (> 20 ppm/yr). Lower uptake rates, in which data exhibited the "leveling off" effect described earlier, tended to best fit logarithmic curves. Despite this, the calculated absorption rates from regression equations correlated very well with observed uptake.

The predictive model for hydrogen uptake rates was intended to supplement regression analysis data in determining long-term effects of grade 12 titanium exposure to alkaline brine solutions. The model also revealed that it is increased corrosion rates, rather than HUE, responsible for the significantly higher uptake rates in saturated NaCl at pH $\geq$ 12.5. The predictive model confirms actual uptake results that suggest long-term pH 12.5 brine solution exposure poses a hydrogen embrittlement concern for grade 12 titanium.

### Practical Guidelines

Hydrogen embrittlement, in terms of measurable loss of mechanical integrity, has been found to occur in grade 12 titanium at levels above about 300 ppm.[9] Assuming a base level hydrogen content of about 50 ppm, the critical threshold level of hydrogen uptake can be targeted at about 250 ppm. Thus, to ensure 20 year service life, hydrogen uptake rates should be no higher than about 12.5 ppm/yr for a thin wall (0.89mm) sheet or tube. Hydrogen uptake rates are inversely proportional to wall thickness, so as wall thickness increases, absorption rates fall. For example, at a 6.35mm wall, the hydrogen uptake rate for grade 12 titanium exposed to natural brine at pH 12 and 107°C, drops to 1.5 ppm/yr. Thus, the concern for excessive hydrogen uptake and possible embrittlement will generally be limited to thin wall material. From this study, it is clear that grade 12 titanium will perform well in brine solutions at pH $\leq$ 12.0. Above this pH level, grade 12 titanium can be subject to excessive hydrogen uptake and possible embrittlement. Thermal oxidation may inhibit hydrogen uptake in pH 12.5 brine, allowing successful application of grade 12 titanium in natural brines. However, in saturated NaCl, thermal oxidation offers no real benefit.

## CONCLUSIONS

1. Grade 12 titanium exhibits on the order of 10 ppm/yr (1mm gage) hydrogen uptake rates in brine solutions with pH $\leq$ 12.0. Increasing wall thicknesses will reduce the uptake rate proportionately.

2. Brine solutions with pH ≥ 12.5 appear to significantly increase hydrogen absorption rates for grade 12 titanium, rendering it susceptible to long-term hydrogen embrittlement. Thermal oxidation may effectively inhibit against hydrogen uptake, however, its effectiveness is dependent on brine composition.

3. Predicted hydrogen uptake rates based on short-term electrochemical tests, offer reliable assessments for long-term performance of grade 12 titanium in hot alkaline brine solutions.

4. Corrosion rates of grade 12 titanium increase by over a factor of 2 when the alloy is exposed to saturated NaCl at pH ≥ 12.5, as opposed to a natural brine at the same pH levels.

## ACKNOWLEDGEMENT

The authors wish to acknowledge the contribution of R. W. Schutz, formerly of TIMET.

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## Table 1

### Hydrogen Uptake Results for Grade 12 Titanium in Natural Brine[1] at 107°C

| Exposure Time (Wks) | Media pH | Avg. Hydrogen Uptake (ΔH) As-Pickled (ppm) | Thermally Oxidized (ppm) |
|---|---|---|---|
| 4 | 12.0 | 3 | 12 |
| 4 | 12.5 | 23 | 6 |
| 4 | 13.0 | 20 | 17 |
| 6 | 12.0 | 8 | 9 |
| 6 | 12.5 | 22 | 11 |
| 6 | 13.0 | 44 | 12 |
| 8 | 12.0 | 4 | 11 |
| 8 | 12.5 | 20 | 11 |
| 8 | 13.0 | 69 | 21 |
| 26 | 12.0 | 21 | 30 |
| 26 | 12.5 | 46 | 16 |
| 52 | 12.0 | 25 | 16 |
| 52 | 12.5 | 47 | 13 |
| 78 | 12.0 | 29 | 26 |
| 78 | 12.5 | 56 | 22 |

[1] Composition: 21% NaCl, 5% KCl, 3.7% $Na_2SO_4$.

## Table 2

### Hydrogen Uptake Results for Grade 12 Titanium in Natural Brine[1] at 121°C

| Exposure Time (Wks) | Media pH | Avg. Hydrogen Uptake ($\Delta H$) As-Pickled (ppm) | Thermally Oxidized (ppm) |
|---|---|---|---|
| 4 | 12.0 | 7 | 8 |
| 4 | 12.5 | 11 | 15 |
| 4 | 13.0 | 81 | 3 |
| 8 | 12.0 | 15 | 3 |
| 8 | 12.5 | 15 | 9 |
| 8 | 13.0 | 62 | 33 |
| 26 | 12.0 | 18 | 3 |
| 26 | 12.5 | 19 | 0 |
| 52 | 12.0 | 18 | 16 |
| 52 | 12.5 | 27 | 27 |
| 78 | 12.5 | 33 | 8 |

[1] Composition: 21% NaCl, 5% KCl, 3.7% $Na_2SO_4$.

## Table 3

### Hydrogen Uptake Results for Grade 12 Titanium in Saturated NaCl at 107°C

| Exposure Time (Wks) | Media pH | Avg. Hydrogen Uptake (ΔH) As-Pickled (ppm) | Avg. Hydrogen Uptake (ΔH) Thermally Oxidized (ppm) |
|---|---|---|---|
| 4 | 12.0 | 16 | - |
| 4 | 12.5 | 36 | - |
| 4 | 13.0 | 376 | - |
| 12 | 12.0 | 12 | 15 |
| 12 | 12.5 | 84 | 8 |
| 12 | 13.0 | 773 | 12 |
| 26 | 12.0 | 17 | 9 |
| 26 | 12.5 | 98 | 26 |
| 26 | 13.0 | 891 | 30 |
| 52 | 12.0 | 23 | 25 |
| 52 | 12.5 | 440 | 180 |
| 78 | 12.0 | 31 | 11 |
| 78 | 12.5 | 324 | 108 |

## Table 4

### Hydrogen Absorption Rates for Grade 12 Titanium From Regression Analysis of Caustic Brine Exposure Results

| Brine Media | Temperature (°C) | pH | Surface Condition | Hydrogen[3] Absorption Rate (ppm/yr) | Actual Uptake[4] After 1 Yr (ppm) |
|---|---|---|---|---|---|
| Natural Brine[1] | 107 | 12.0 | As-Pickled | 12 | 11 |
| " | 107 | 12.5 | As-Pickled | 24 | 21 |
| " | 107 | 12.0 | T.O.[2] | 11 | 8 |
| " | 107 | 12.5 | T.O. | 9 | 7 |
| " | 121 | 12.0 | As-Pickled | 10 | 9 |
| " | 121 | 12.5 | As-Pickled | 13 | 12 |
| " | 121 | 12.0 | T.O. | 7 | 8 |
| " | 121 | 12.5 | T.O. | 7 | 8 |
| Saturated NaCl | 107 | 12.0 | As-Pickled | 12 | 11 |
| " | 107 | 12.5 | As-Pickled | 141 | 164 |
| " | 107 | 12.0 | T.O. | 8 | 8 |
| " | 107 | 12.5 | T.O. | 50 | 63 |

[1] Composition: 21% NaCl, 5% KCl, 3.7% $Na_2SO_4$.

[2] Thermally Oxidized.

[3] Calculated from linear regression analysis equations. Assumes 0.9mm wall thickness and single side exposure.

[4] Yearly average based on 52 and 78 week results, corrected for single size exposure.

## Table 5

### Predictive Model for Hydrogen Uptake Rates in Grade 12 Titanium

| Brine Media (107°C) | pH | HUE (%) | Corrosion Rate (Linear Polarization) (mm/yr) | Predicted Uptake (ppm/yr) | Actual Uptake[2] After 1 Yr. (ppm) |
|---|---|---|---|---|---|
| Natural Brine[1] | 12.0 | 27 | $5.1 \times 10^{-4}$ | 13 | 11 |
| Natural Brine | 12.5 | 26 | $1.3 \times 10^{-3}$ | 31 | 21 |
| Sat. NaCl | 12.0 | 24 | $5.1 \times 10^{-4}$ | 12 | 11 |
| Sat. NaCl | 12.5 | 26 | $2.8 \times 10^{-3}$ | 69 | 164 |

[1] Composition: 21% NaCl, 5% KCl, 3.7% $Na_2SO_4$.

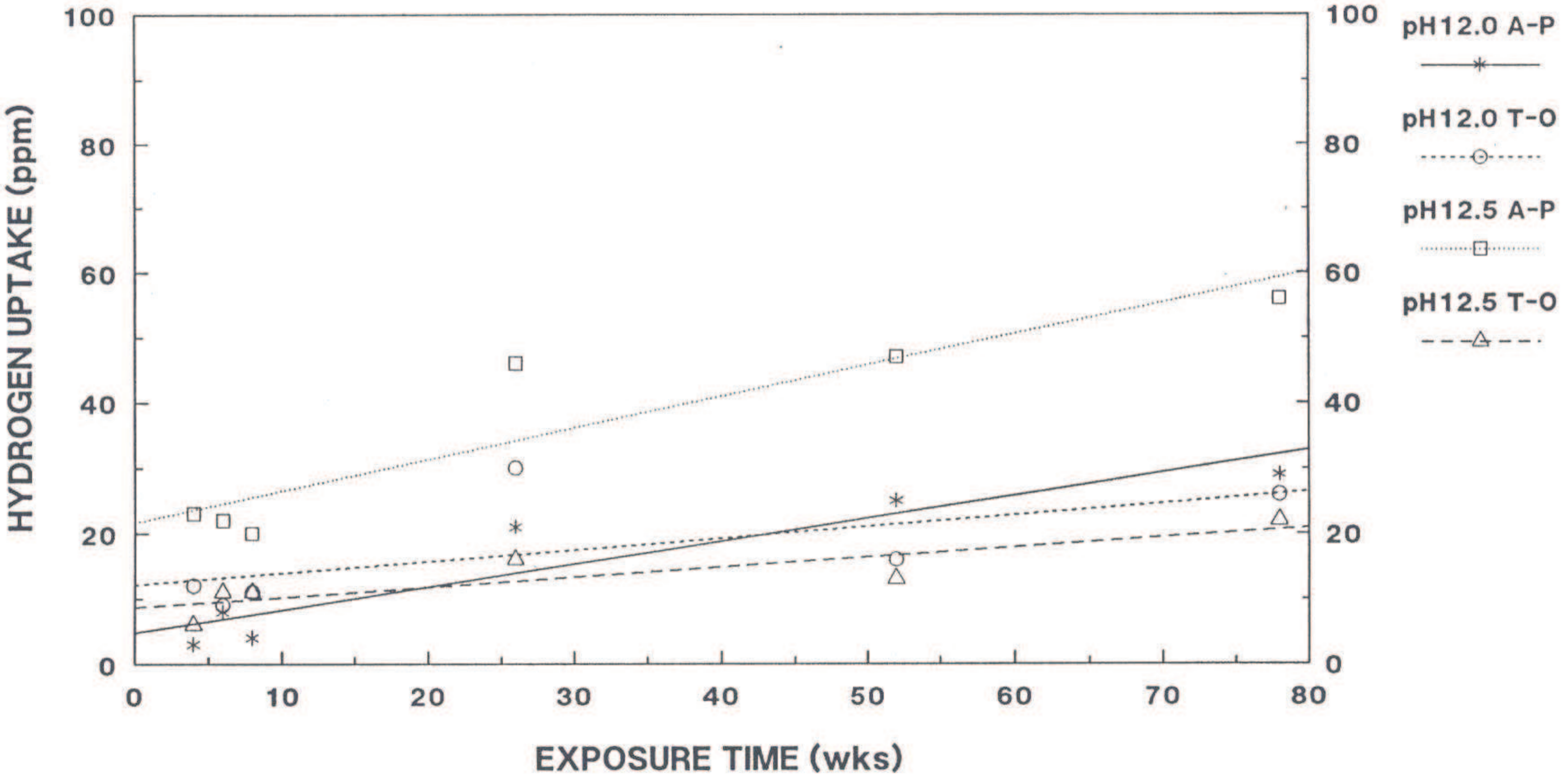
[2] Yearly average based on 52 and 78 week results, corrected for single side exposure.

Figure 1

## HYDROGEN UPTAKE ON GRADE 12 TITANIUM

### IN NATURAL BRINE AT 107 C

### LINEAR REGRESSION ANALYSIS



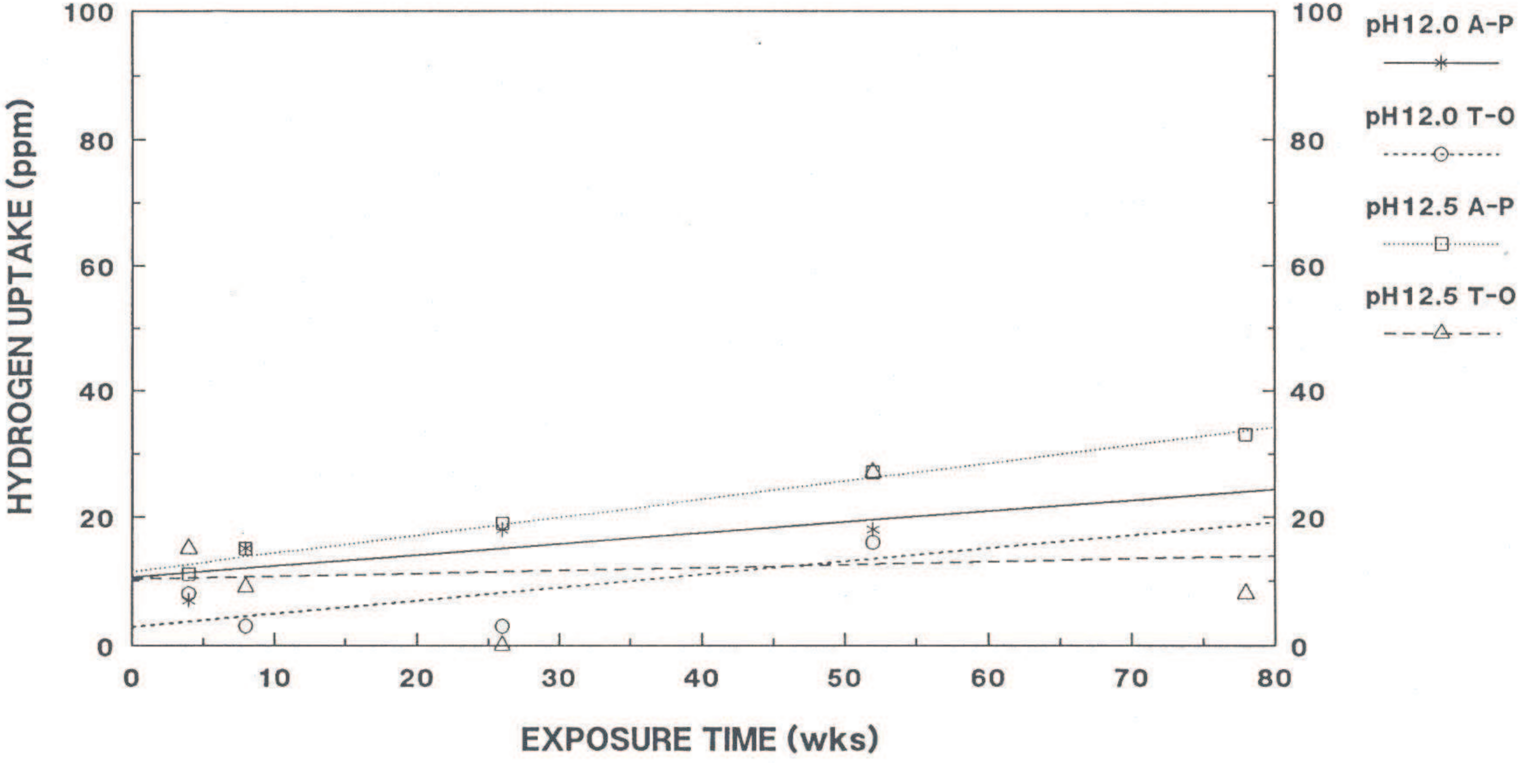
A-P : AS PICKLED SURFACE COND.
T-O : THERMALLY OXIDIZED SURFACE COND.
BRINE COMP.: 21%NaCl, 5%KCl, 3.7%$Na_2SO_4$

Figure 2

HYDROGEN UPTAKE ON GRADE 12 TITANIUM

IN NATURAL BRINE AT 121 C

LINEAR REGRESSION ANALYSIS



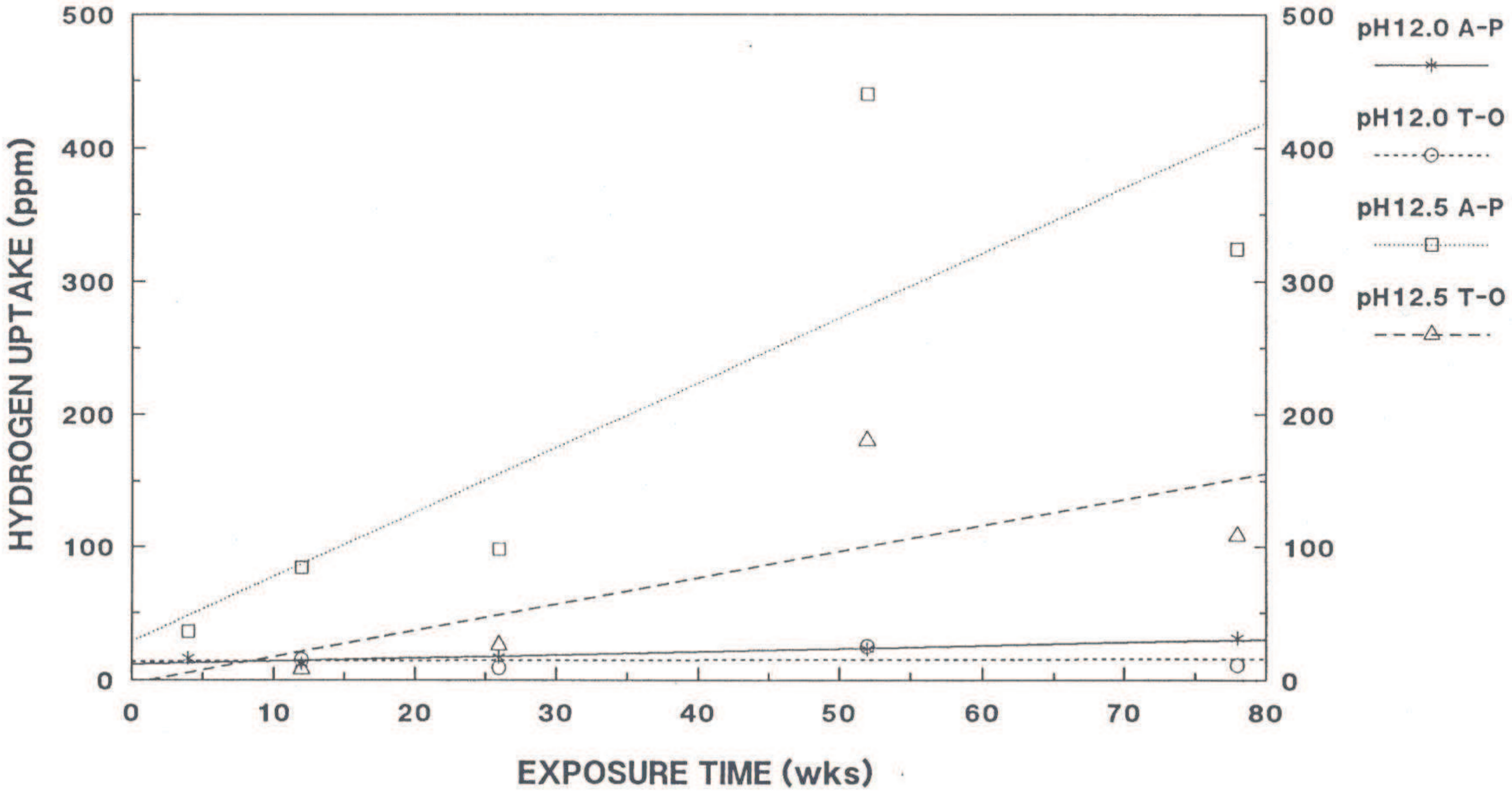
A-P : AS PICKLED SURFACE COND.
T-O : THERMALLY OXIDIZED SURFACE COND.
BRINE COMP.: 21%NaCl, 5%KCl, 3.7%$Na_2SO_4$

Figure 3

# HYDROGEN UPTAKE ON GRADE 12 TITANIUM

IN SATURATED NaCl AT 107 C

LINEAR REGRESSION ANALYSIS



A-P : AS PICKLED SURFACE COND.
T-O : THERMALLY OXIDIZED SURFACE COND.

## FIFTH INTERNATIONAL MEETING ON TITANIUM

# APPLICATIONS FOR CAST TITANIUM COMPONENTS IN THE PROCESS INDUSTRY

By :-

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## INTRODUCTION

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

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

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

## PHYSICAL PROPERTIES

Whilst there is a wide range of wrought titanium alloys available there is only need to consider three for use as castings in the process industries. Their chemical compositions are given in Table 1.

Table 1

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

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

Table 2

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

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

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

Table 3

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

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

## CASTING TECHNIQUES

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

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

b) Low fluidity of the metal at pouring temperatures.

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

These problems have now been overcome by:

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

ii) Centrifugal pouring.

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

Normally titanium in the form of consumable electrode is arc melted in a vacuum. The melting crucible is a double walled copper container with water cooling which causes a solid skull of titanium to be formed on the inner surface. This skull and the absence of an atmosphere protects the molten metal from contamination. When the electrode has been consumed the metal must reach the moulds as quickly as possible. This is achieved by the use of a centrifugal pouring arrangement which is shown. schematically in Figure 1.

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

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

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

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

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

Table 4

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

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

Table 5

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

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

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

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

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

## MACHINING

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

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

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

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

d) Prevent vibration by using large rigid machines.

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

Table 6

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

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

## WELDING

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

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

## COST CONSIDERATION

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

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

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

Table 7

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

## Corrosion Resistance

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

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

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

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

## Hydrochloric Acid

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

## Nitric Acid

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

## Wet Chlorine

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

(a) Manufacture of chlorine

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

(c) Bleaching of pulp in the paper industry.

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

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

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

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

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

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

Table 8

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

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

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

Table 9

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

## Sea Water

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

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

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

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

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

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

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

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

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

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

## Case Histories and Service Experience

### 1. Nylon Manufacture

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

### 2. Sea Water

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

### 3. Caustic/Chlorine Production

#### (a) Chlorine Absorption

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

#### (b) Chlorine Treatment

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

4. Brine Transfer

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

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

5. Caustic/Chlorine Plant

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

6. Steel Pickling Plant

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

7. Bleach Solutions

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

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

Table 10

| Material | Cost Factor |
|---|---|
| 316L Stainless Steel | 0.8 |
| 317L Stainless Steel | 1 |
| 254 SMO | 1.3 |
| Titanium | 1.8 |

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

Titanium pumps are becoming a standard component for handling chlorine dioxide liquors in bleach plants and scanpump of Sweden alone have supplied more than 100 pumps between 1980 and 1982 all of which are still operating without any significant deterioration due to corrosion. The sizes range from a capacity of 10m$^3$/h with a 10m head (50mm inlet/40mm outlet with a 160mm impeller) to 120m$^3$/h with a 50m head (150mm inlet/125mm outlet with a 400mm impeller).

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

## Conclusions

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

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

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FIGURE 1

# CENTRIFUGAL CASTING

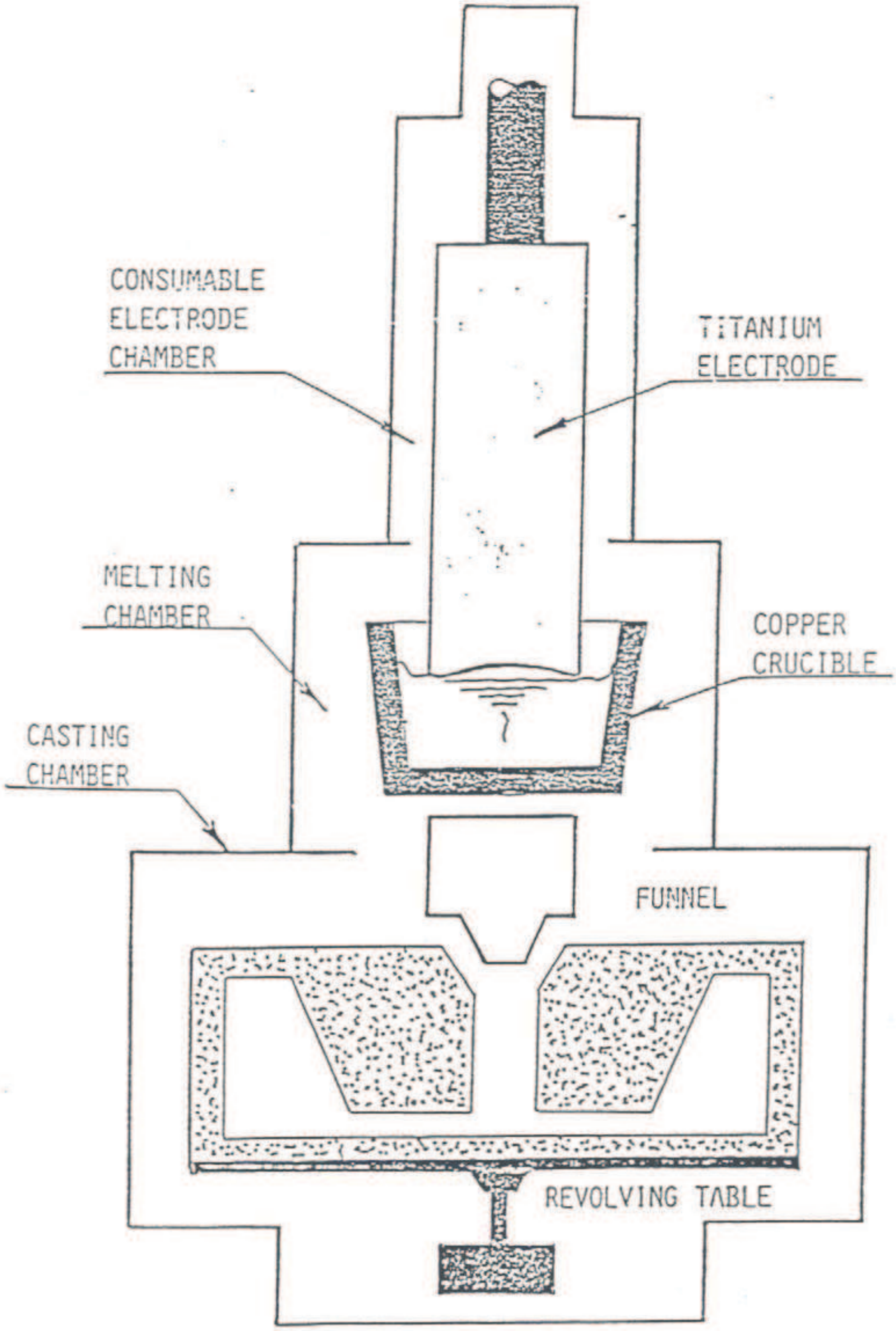
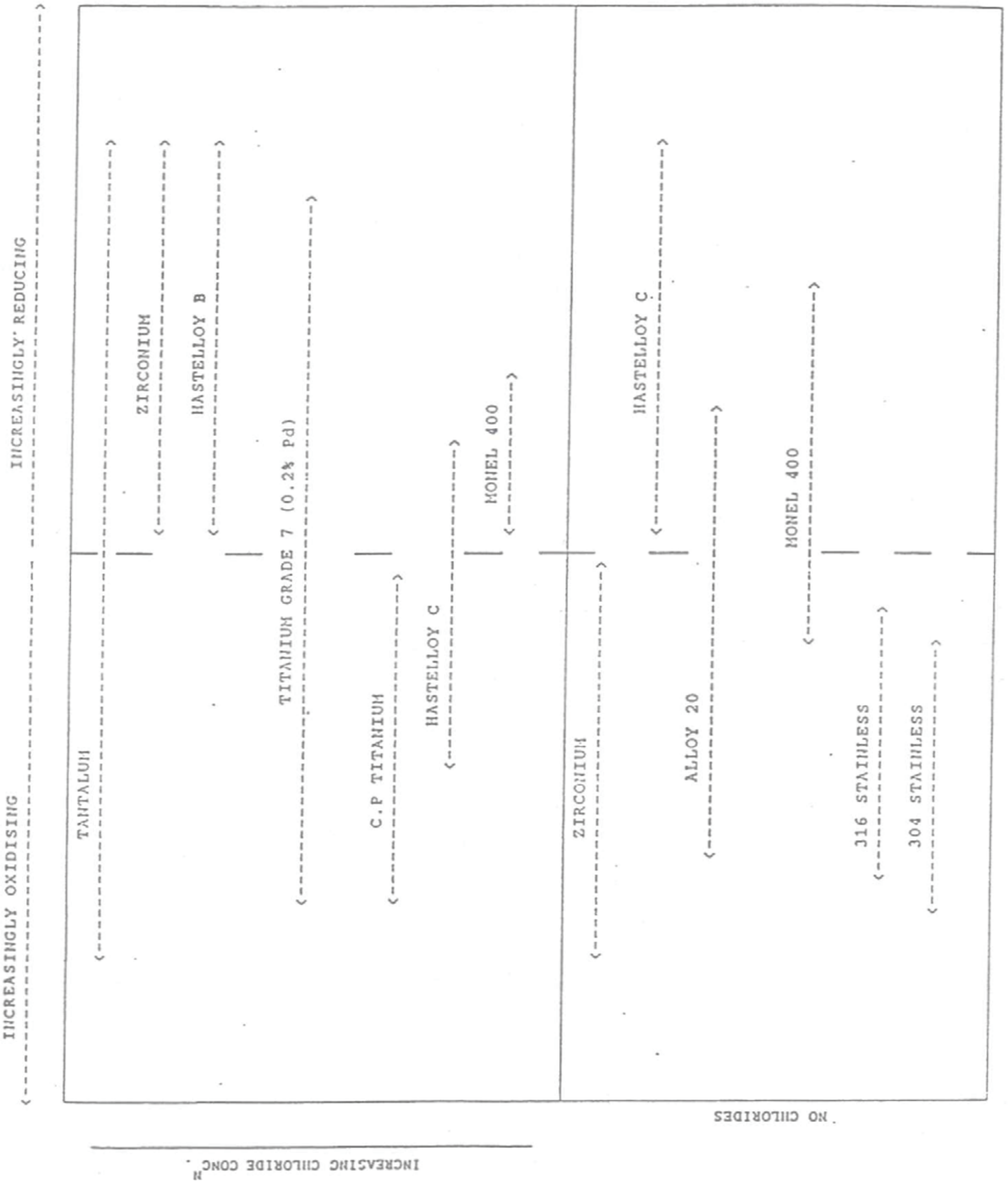
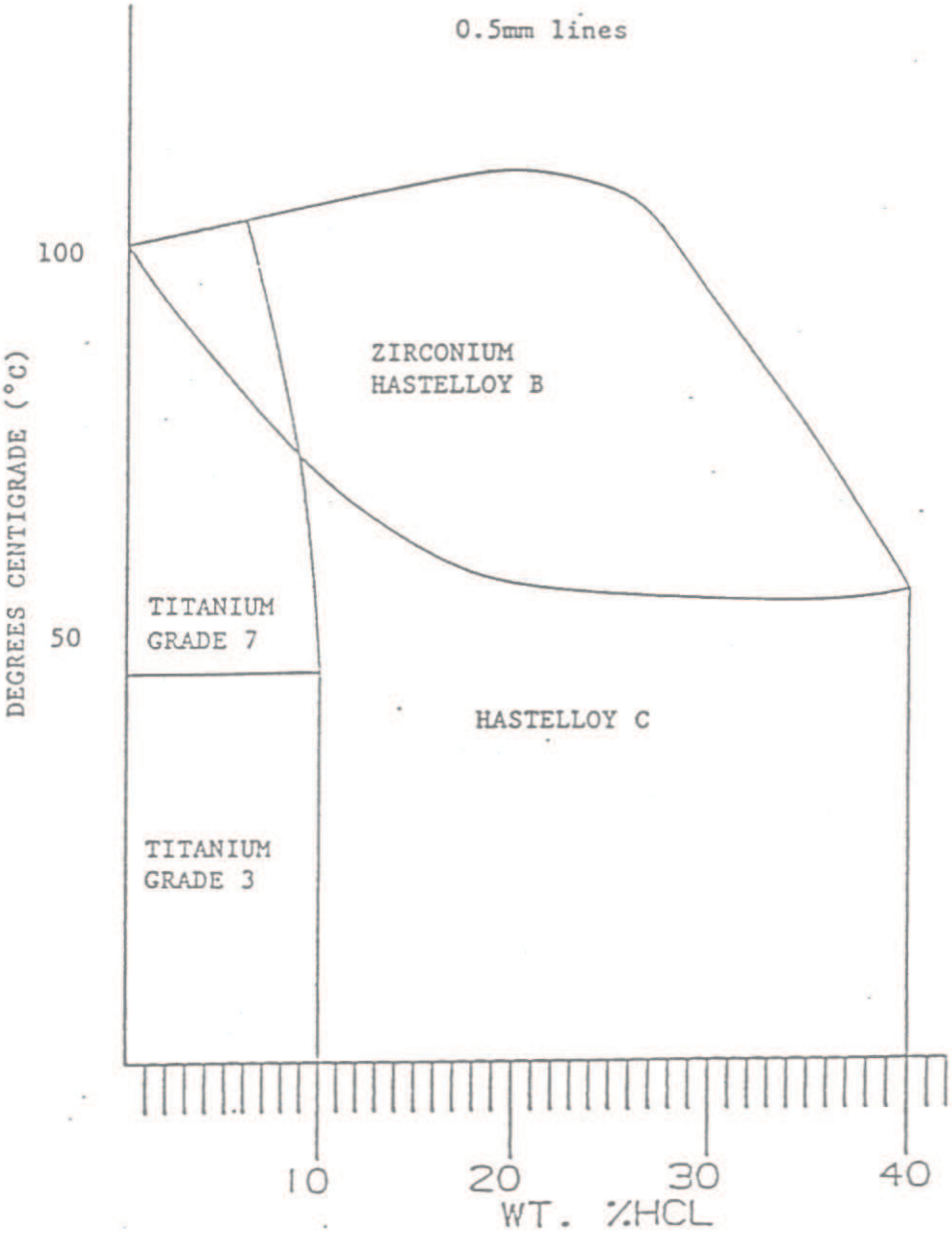


FIGURE 2



SCHEMATIC CORROSION CHART

FIGURE 3



HYDROCHLORIC ACID ISOCORROSION CHART

# Esempi di nuove applicazioni del titanio realizzate da GTT in collaborazione con industrie ed enti italiani.

Ezio Debernardi - GTT - Torino

Signore e Signori buon pomeriggio.

Questo è ormai il quinto anno consecutivo in cui Vi presentiamo i risultati di nuove applicazioni industriali del titanio, realizzate in collaborazione con industrie italiane, e le linee di attività del Settore Metallurgia della GTT.
Quest'anno è stato caratterizzato da una vivace attenzione da parte di numerosi enti ed industrie nei confronti del titanio, che inizia a non essere più considerato un metallo per applicazioni sofisticate, bensì un normale materiale a cui ricorrere per risolvere in modo sempre più professionale le problematiche industriali.
Come potete vedere dalla fotocopia del giornale "Il Messaggero" di oggi, che Vi è stata distribuita, un ultimissimo esempio è il restauro della Fontana di Trevi.
In realtà i contatti sono iniziati già da tempo, perchè il problema è molto complesso.
Altri esempi di questa crescente attenzione da parte dell'industria italiana nei confronti del titanio sono stati: l'interesse rivoltoci dall'AIMAN (Associazione Italiana di Manutenzione) che ha riservato quest'anno al titanio e alle sue leghe ben due momenti: uno durante il XIII congresso nazionale l'altro durante una giornata di studio sull'uso di materiali innovativi e migliorativi per la manutenzione.

Altra testimonianza di spontaneo interesse nei confronti del titanio ci è stata fornita durante la nostra partecipazione al 29° Salone Nautico di Genova. In questo caso siamo stati letteralmente "bombardati" da parte della cantieristica e dell'indotto navale con una serie di quesiti riguardanti soprattutto la resistenza alla corrosione in acqua di mare, la leggerezza, l'amagneticità, la resistenza alla cavitazione ed all'erosione, ecc. cioè tutte quelle problematiche a cui titanio e sue leghe danno una soluzione definitiva.

Vediamo ora qualche concreta collaborazione portata a termine nel corso di questo anno.

Abbiamo continuato la nostra esperienza nel settore della robotica industriale; sempre in collaborazione con la Società Gerbi di Torino abbiamo realizzato una pinza per robot di saldatura (fig. 1) destinata ad una nuova linea di assemblaggio scocche per veicoli commerciali.
L'obiettivo era quello di mettere a punto una struttura la più leggera possibile ma estremamente resistente a fatica (il carico preventivato sugli elettrodi a chiusura è di 400 kg) (fig. 2).
Da notare le dimensioni: la lunghezza dei bracci è di 1100 mm (fig. 3) e la distanza tra i due bracci in posizione di chiusura è di circa 600 mm (fig. 4).
Il manufatto è stato realizzato mediante una carpenteria saldata del peso complessivo di 35 kg, utilizzando lamiere di spessore pari a 5 mm in lega Ti 6Al-4V.
Il peso della pinza in opera è di circa 90 kg.

La seguente realizzazione (fig. 5) ha voluto dare una risposta alle esigenze dei costruttori di cilindri oleodinamici che operino in ambienti corrosivi. In collaborazione con la Soc. ICO di Modena, abbiamo costruito una serie prototipale del modello che è anche visibile presso il nostro stand.
Vediamo alcuni dati costruttivi:
alesaggio 80 mm (fig. 6)
dia. stelo 45 mm
corsa di 500 mm
pressione di lavoro tra i 250 e i 270 bar, con un valore di pressione di collaudo pari a 375 bar.
Materiale impiegato è nuovamente la lega Ti 6Al-4V sotto forma di tubo estruso, barre, piatti (fig. 7).

E’ importante rilevare che le caratteristiche richieste a questi manufatti oltre alla resistenza alla corrosione ed alla tensio corrosione sono:
- leggerezza
- amagneticità
- basso coefficiente di dilatazione termica
- resistenza a fatica

Le applicazioni di tali prodotti sono molte, l’esigenza è nata dalla richiesta di sistemi di comando per portelli di traghetti e per paratie di chiuse fluviali; ma non bisogna dimenticare le installazioni marine in genere, con particolare interesse ai sistemi su off-shores.

Ora vorrei brevemente indicarVi le attività future della sezione Metallurgia.

Come già annunciatoVi lo scorso anno, presso il nostro stabilimento di Santena è stato installato un impianto fusorio V.A.R. (fig. 8 e 9).

Dopo la messa a punto e l'ottimizzazione della procedura di fusione di lingotti in titanio Cp e leghe classiche come la Ti 6Al-4V, ci accingiamo ad affrontare alcuni programmi piuttosto impegnativi:

- preparazione delle cosiddette "leghe a memoria di forma" a base Ti-Xi.
- la preparazione di leghe superconduttrici a base Ti-Nb.
- preparazione di composti intermetallici Ti-Al, i cosiddetti alluminiuri.

Le dimensioni e la versatilità di tale impianto, permettono il suo utilizzo anche per la produzione pilota di leghe sperimentali (fig. 10).

Attualmente questi argomenti godono di uno spiccato interesse sia dal punto di vista della ricerca che nel campo delle applicazioni industriali.

Per quanto riguarda le leghe a memoria di forma ed i superconduttori Nb-Ti si ricorda che questi prodotti sono già commercializzati da un numero limitato di produttori. Infatti le Ni-Ti sono prodotte, attualmente, sia dalla giapponese FuroKawa che dalla Raychem americana, mentre le Ti-Nb sono prodotte nel mondo solo dalla Teledyne Wa-Chang negli USA.

Quindi a fronte di un crescente interesse da parte del mercato, si ritiene opportuno investigare e mettere a punto il sistema di produzione a livello pilota di tali prodotti.

Dal punto di vista applicativo ricordiamo che le leghe a memoria di forma di tipo Ti-Ni, trovano un crescente impiego in svariati campi: dal biomedico ed ortodontico, all'occhialeria, a dispositivi di attuatori per l'industria elettronica, elettromeccanica ed automobilistica.

I superconduttori Ti-Nb continuano, nonostante la scoperta dei superconduttori ceramici, ad alta temperatura critica, ad essere utilizzati in crescenti quantità nella generazione di campi magnetici.

In questo settore siamo impegnati nel Programma Finalizzato "Tecnologie Super Conduttive e Criogeniche" del CNR, che prevede lo studio e la messa a punto del processo di fabbricazione su territorio nazionale di questi prodotti.

I sistemi intermetallici Ti-Al sono oggetto di approfondite ricerche in numerosi laboratori specializzati.
Questo tipo di leghe permetteranno, una volta messe a punto, di ampliare il campo di utilizzo delle leghe di titanio verso più alte temperature di esercizio. Si prevede che il limite attuale dei 550 - 600°C verrà innalzato, in fasi successive, sino a temperature dell'ordine degli 800 - 900°C.

In collaborazione con l'Istituto per Materiali Metallici Non Tradizionali del CNR si sono affrontate le problematiche di fabbricazione di questi sistemi.
Pensiamo di proseguire la sperimentazione, indagando sulle tecnologie di fusione e sulle possibilità di lavorazioni plastiche di tali materiali.

## Conclusioni

Ho voluto illustrarVi le linee di sviluppo delle nostre attività, poichè la GTT ritiene che in questo lavoro esistano le premesse per un riscontro pratico molto importante.
Infatti queste attività si concretizzano in un’azione costante nel tempo di supporto al Marketing Tecnico del Mercato del Titanio.
Riteniamo giusto dare un servizio alla clientela, presente e futura, in modo tale che possa affrontare e risolvere problematiche tecniche sempre più complesse, in modo semplice ed affidabile.

Grazie.

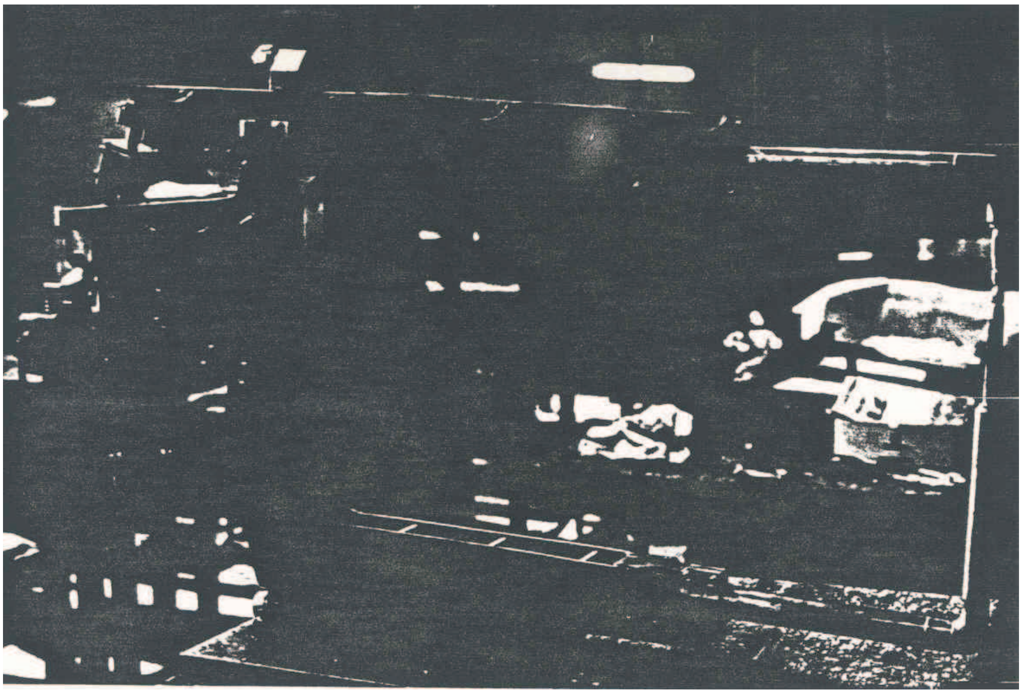


Fig. 1 - Pinza per robot di saldatura

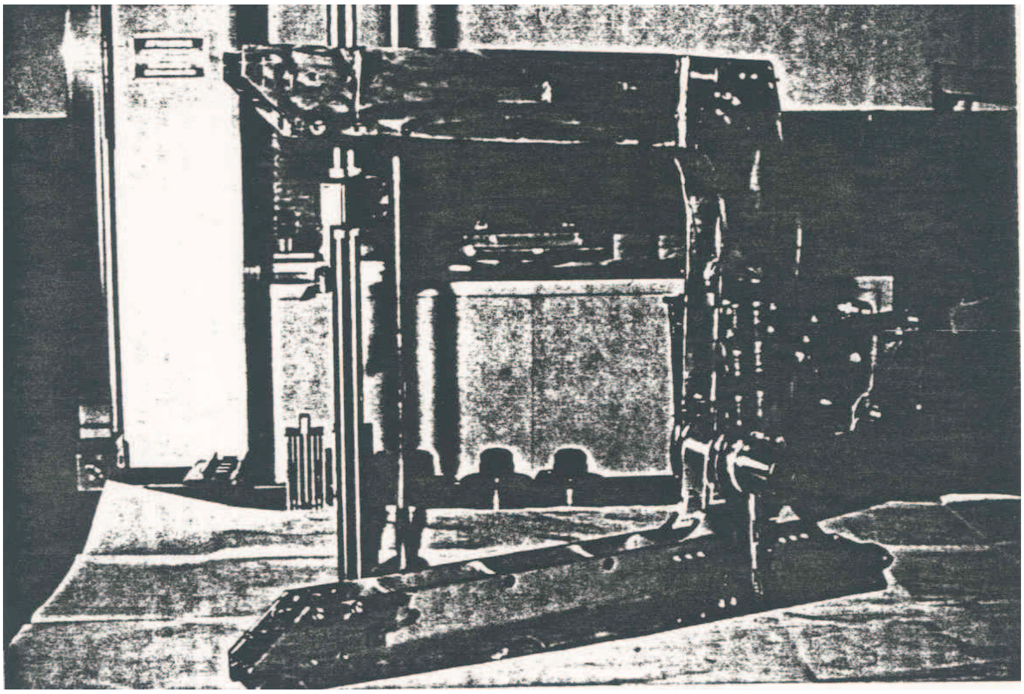


Fig. 2 - Struttura della pinza di saldatura in lega di Ti-6Al-4V

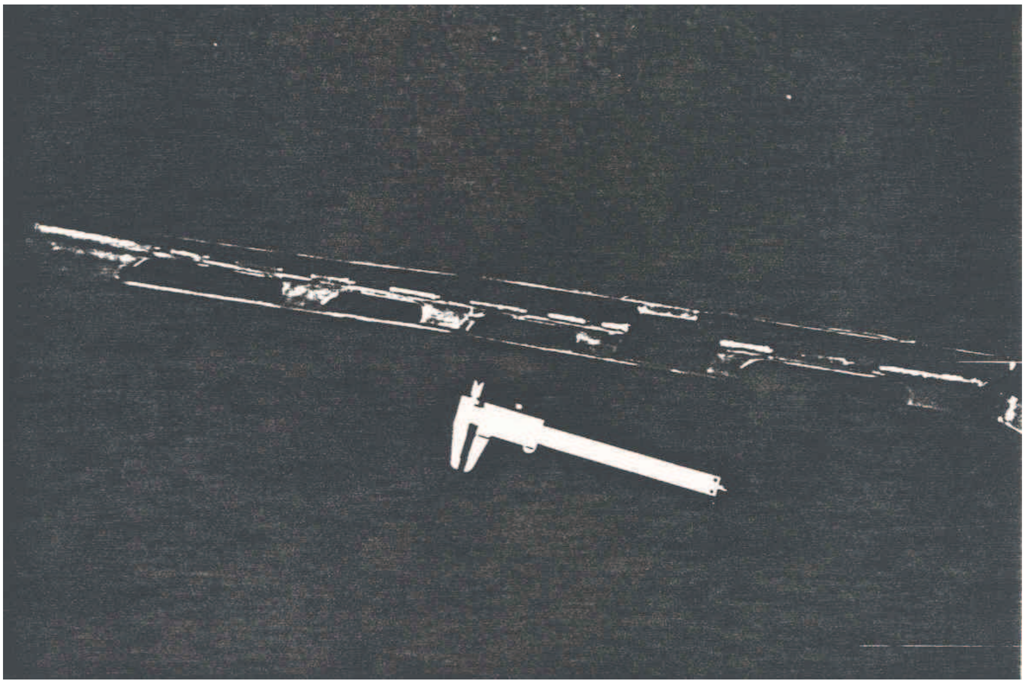
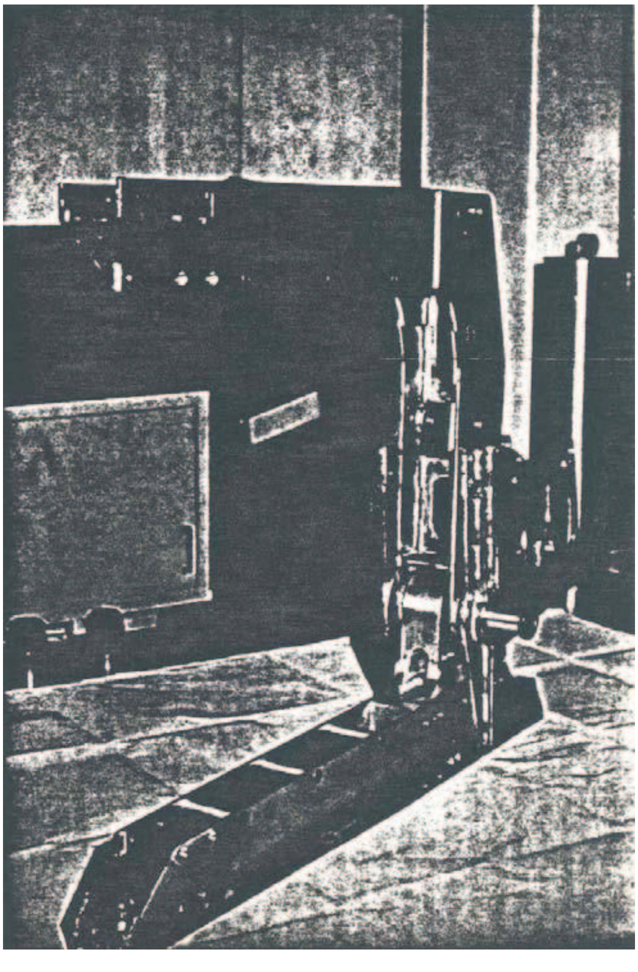


Fig. 3 - Braccio della pinza di saldatura

Fig. 4

Struttura della pinza

in posizione di chiusura



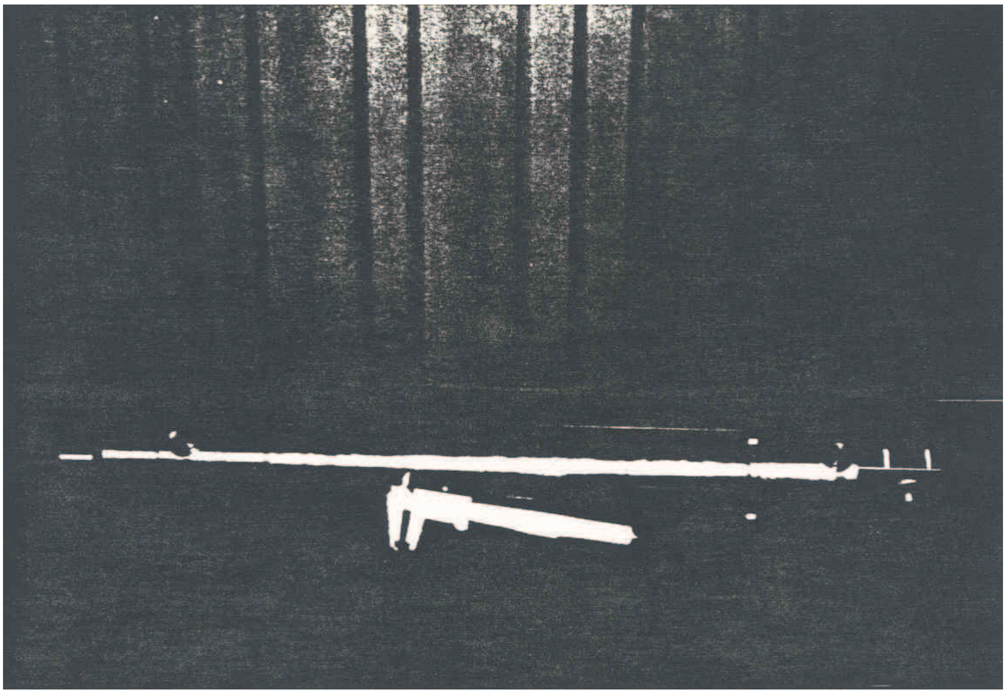


Fig. 5 - Cilindro oleodinamico in lega di Titanio per ambienti corrosivi

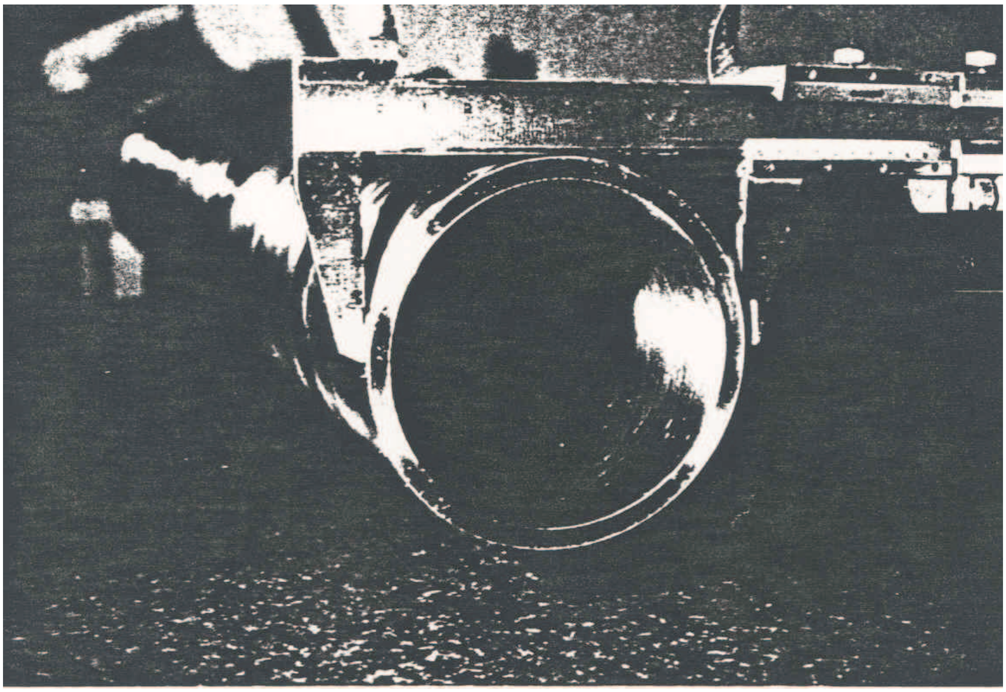


Fig. 6 - Tubo estruso in lega Ti-6Al-4V per il corpo cilindrico

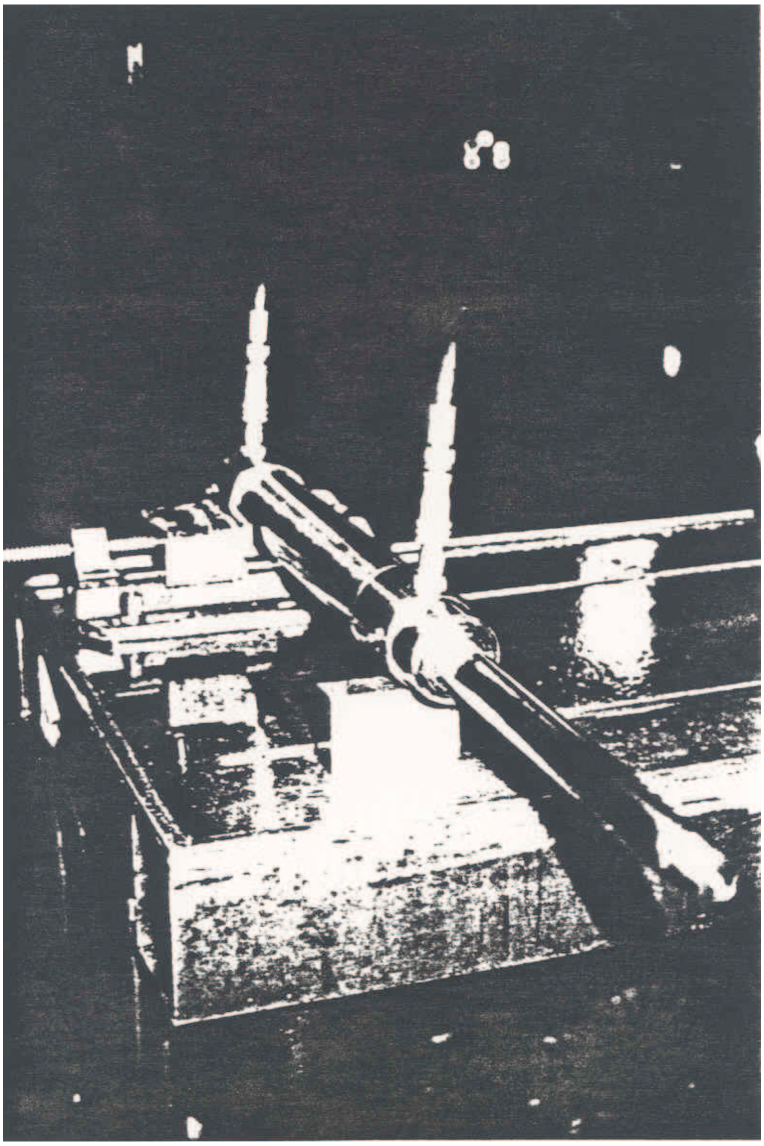


Fig. 7 - Fase di collaudo del cilindro

Fig. 8

Impianto fusorio V.A.R.

(Vacuum Arc Remelting)

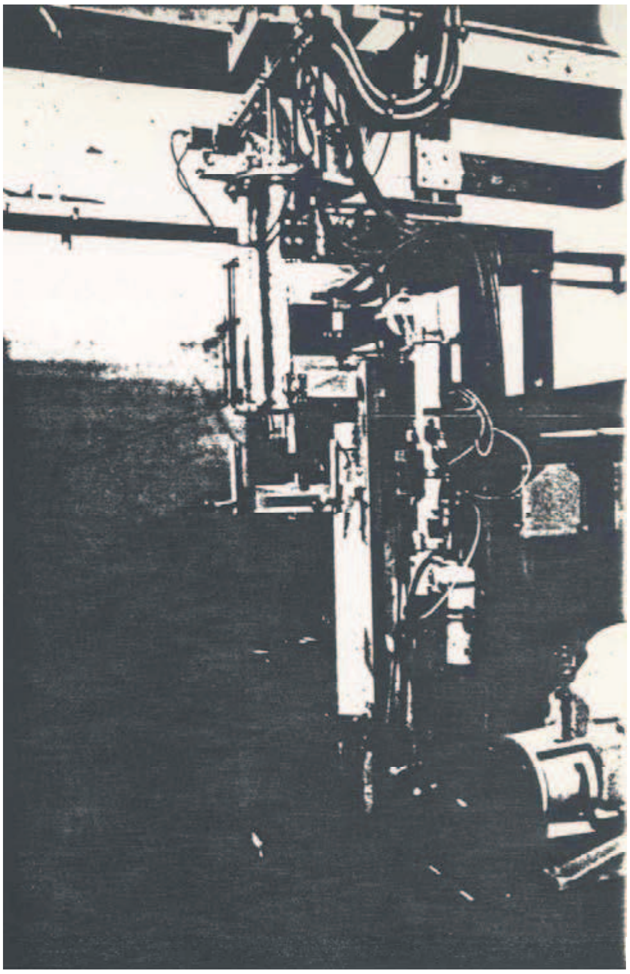


Fig. 9

Consolle di comando del

Forno

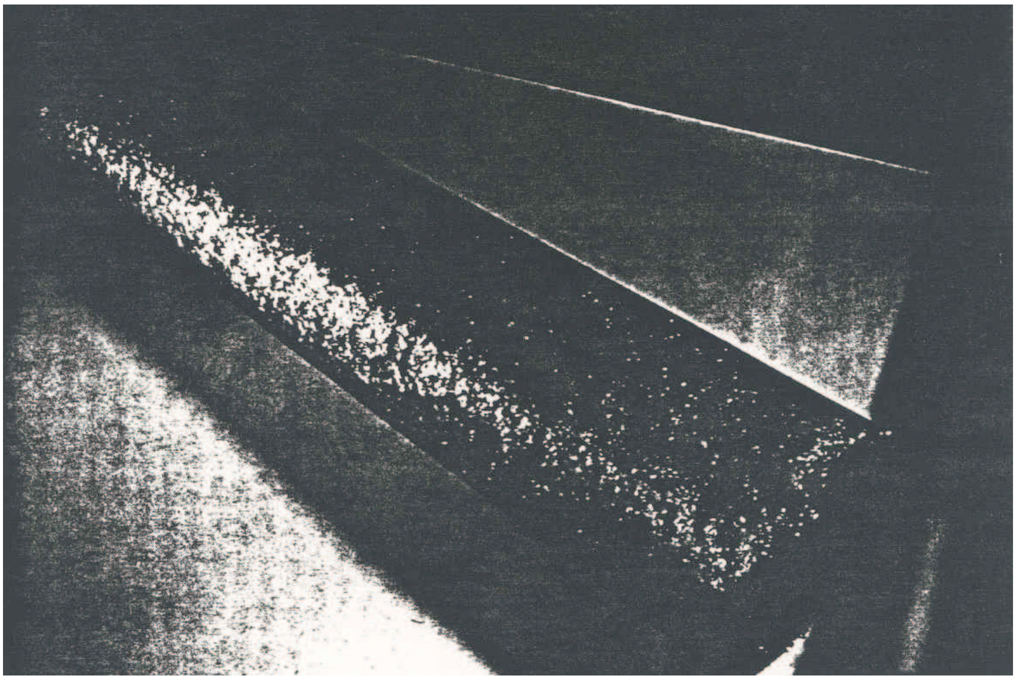


Fig. 10 – Lingotto in lega di Titanio fuso nell'impianto V.A.R.
(dimensioni: dia. 200 mm – altezza 1000 mm)

# SAVE COSTS - USE INVESTMENT CASTING

Dr. Ch. Liesner
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## INTRODUCTION

In Titanium investment casting a very old moulding procedure and a young material have made products possible which are unique in their properties.

Increasing demands and requirements of technique and manufacturing industry are:

- optimal material use
- complicated shapes
- independence from quantity
- high dimensional accuracy
- casting ready to be installed
- functional small wall thicknesses

All these requirements are fulfilled at investment casting to the lost wax process with lost models. One further advantage of investment casting is expressed with the slogan, investment casters advertise with: “use investment castings - save costs”.

## APPLICATIONS OF TITANIUM CASTINGS

Essentially there are two typical properties of Titanium and its alloys, which impose its application and which are not equalled by other materials in any other way:

a) Great performance ratio from mechanical properties to specific gravity. This property makes Titanium and its alloys in great demand for aircraft and aerospace industries. Titanium investment castings are used in power units, at high stressed planks and mountings, airframe elements and further applications (Fig. 1).

The high solidity at low specific gravity of Titanium opens further applications in these areas where high mass forces due to great accelerations must be avoided. Representative of these are textile machines, centrifuges, turbo exhausters, where steel investment casting is more and more substituted by Titanium investment castings.

b) Excellent corrosion resistance against oxidizing media. Applications are in chemical installation for investment castings, pump housings, pump impellers, valves, manifolds and similar elements.

Further application are also implants in the medical field such as: implants as teeth roots, joint implants etc. Titanium is one of the few bio-compatible materials which are accepted by the body without mutual reactions and repulsion reactions. There are in process additional developments of alloys for implantation medicine (Fig. 2).

## CASTING PROCESS

For several reasons, including the very high reactivity of molten titanium with other materials, casting is a particularly specialised process.

A consumable-electrode method of vacuum melting is employed, special mold materials are used, and the molds are usually spun in a centrifuge during pouring in order to ensure that the molds are completely filled.

Mold techniques are similar to those used for casting other metals.

Because of the mechanical properties of cast titanium and its alloys are very close to those of wrought material, castings can be used for critical structural parts.

The ability to cast complex shapes to close tolerances and with good surface finish results in:
high material utilisation, reduced machining costs, welded and mechanical joints avoided by casting shapes that cannot be machined from a single piece of metal, improved strength and stiffness or equivalent weight reduction by casting hollow or deeply-ribbed shapes.

Therefore, any parts that could benefit from any of the above, are usually good candidates for casting.

All alloys can be cast, although CP and Ti-6Al-4V cover most requirements.

Post-casting operations include removal of ingates and risers, etching to remove surface contamination, HIP treatment when appropriate, inspection including X-ray and penetrant, and quality control including chemical analysis and tensile tests of samples cast with every pour.

## DESIGN PRINCIPLES

While most shapes can be cast, quality and cost-effectiveness are both improved if the design embodies good casting principles. Broadly these are to ensure complete filling of the mold, to avoid shrinkage cavities and porosity, to avoid unnecessary tooling complexity, and to take advantage of the freedom (relative to machining) that casting allows in optimising shapes for structural or other reasons.

Mold filling is facilitated by providing for adequate ingates and risers close to heavy sections, preferably on surfaces that are machined in the finished component (for example joint faces) or that can be fettled to a simple shape. The design should also avoid isolated masses that can only be filled through thin-walled areas.

Shrinkage occurs as metal solidifies. The thinnest sections cool and solidify first, with adjacent molten metal drawn in by the shrinkage. The last parts to solidify are in the centres of the thickest masses, and inevitably this causes the formation of cavities of some sort. By designing the part with sections tapered out to riser faces solidification will progress from thin to thick metal ending in the risers, where cavities are of no importance.

The mold system selected (RG or investment shell) will depend on size, complexity, tolerances and finish required, and production numbers. The part should then be designed to allow the simplest construction of the patterns or dies, with suitable draft angles and with no needless undercuts (which can be made only at the expense of added tooling complexity)

Shapes can be easily cast that would be expensive or impossible to machine from forgings, including deep ribbing to improve the strength or stiffness of the finished component, elimination of unwanted heavy sections, and the inclusion of hollow features. Fig. 3 shows aerospace part these could not reasonably be made than by casting.

Another factor which should be considered in the design of a Titanium casting is the utilization of HIP. The primary stumbling block for the acceptance of more castings in critical applications has been the high level of mechanical property data scatter which is typically encountered with cast material. While the average property levels of cast and wrought material are nearly equivalent, the two sigma minimum design levels are considerably lower for cast material because of the data scatter. Since the designer must use minimum design curves, wrought material is favored in most cases. This is where HIP comes in. The application of high temperature and inert gas pressure to castings produces a twofold change; the casting microstructure is homogenized and internal gas and shrinkage voids are eliminated. Both changes are advantageous in that they reduce mechanical property data scatter. HIP also allows production of components which are not castable from shrinkage and gas defect standpoints. Rejectable, internally detective cast components can be HIP processed into acceptable parts. Internal voids are transformed into dimples on the casting surface which are, in most instances, within blueprint requirements.

Again, and it can’t be overemphasized; the approach to obtaining the optimum casting design is of utmost importance. The casting designer must assume that the designer’s specifications are not flexible, if no communication exists between them. It is only through mutual understanding of performance requirements and casting limitations by both customer and foundry designers that the most cost and performance effective configuration can be achieved.

## COST COMPARISONS

When comparing a cast component with one machined from a forging or other wrought stock, it is important to assess the cost of the finished article.
The casting itself may be of similar cost to the equivalent wrought material, and the real savings are likely to be in reduction or simplification of machining or in avoiding joints by replacing several pieces by a one-piece construction.

If a cast titanium part is compared with one made of a different metal it may be worth assessing life-cycle costs because in some environments one titanium part may outlive several made in another material.

It is not practical to give numerical data on costs because they change continually and because machining costs vary between different companies.

By means of the so-called Spoiler the wing of the Airbus A 310 is hinged and actuated (Fig. 4)

Originally, this integrated “highly stressed” bracket used to be an assembly construction composed of 9 titanium parts that were machined all over and therefore did comply with the very conventional technique applied for the construction of airplanes. The development of foundry technique, especially with regard to the casting of titanium alloys to the “lost wax process”, was the basis for the necessary conditions to manufacture this very intricate component which is well castable tram the point of view of geometrical shape. This very part as a titanium investment casting - the external dimensions are 320. 400. 150 mm - is 100 g lighter. The titanium bracket could be optimized by the investment casting process which has a favourable impact on the fatigue behaviour.

Based on a production quantity of 1128 pieces. important data reveal assembly production of former times and today's manufacture of investment castings. If the eminent difference of 96 % in machining costs (along with assembly costs) can be considered as almost normal - because of “investment” - it is surprising that the material costs differ by 3.5 % only, this in favour of investment casting.

Semi-finished products on the one hand and rough castings ready to be assembled in large lots on the other hand are compared here.
One reason is the much higher material utilisation.
As a matter of fact, the difference in assembly costs of approximatively 86 % is evident. However, since relatively low amounts are involved - 483,- DM and 67,- DM for castings- the influence on the productions costs is not that important. The difference of about 50 % amounts to savings of 6.418,- DM per piece.

HINGING FOR COMPONENT OF WING OF AIRPLANE

| | Formerly | Today |
|---|---|---|
| Production | Assembly | Investment Casting |
| Alloy | Titanium | Titanium |
| Weight | 4500 g | 4400 g |
| Costs for jigs and fixtures and tools respectively | 100 % | 64.6 % |
| Material costs | 100 % | 96.5 % |
| Machining and assembly costs | 100 % | 3.9 % |
| Production costs | 100 % | 50.5 % |

Fig. 2

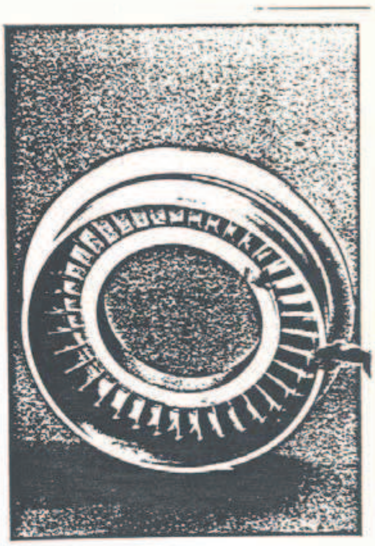


Fig. 1

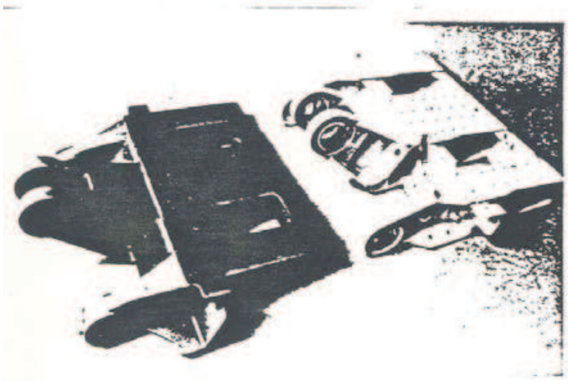


Fig. 4

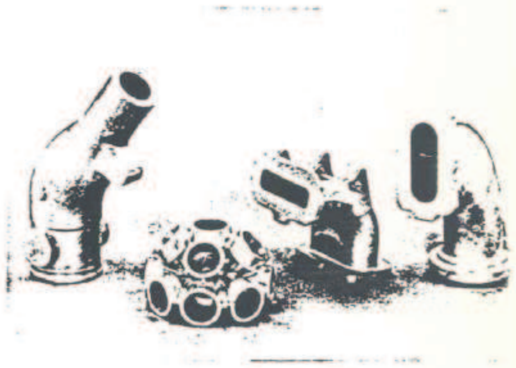


Fig. 3

# ATTIVITA’ INDUSTRIALI E DI RICERCA IN AMBITO ILVA RELATIVE AI PRODOTTI IN Ti

A seguito dell'iniziativa industriale che ha visto la costituzione della Soc. TITANIA, l’ILVA ha iniziato un lavoro di messa a punto dei cicli di lavorazione dei prodotti in Ti avvalendosi dell’impiantistica già esistente, delle competenze dei tecnici di stabilimento e di quelli di ricerca e sviluppo disponibili presso il CSM.

L’impiantistica fondamentale consiste

- per i laminati piani, prodotti presso ILVA-TERNI, di:
  - * forno a $CH_4$ per il riscaldo delle bramme;
  - * laminatoio per nastri a caldo costituito da un quarto reversibile sbozzatore e da sette gabbie finitrici per la fabbricazione di nastri con spessore 3 - 12 mm, larghezza 800 - 1550 mm (Fig. 1);
  - * linee di decapaggio e ricottura e laminatoio a freddo Sendzimir per nastri 0.5 - 3 mm di spessore, da cui è possibile ricavare nastri con larghezza 50 - 1350 mm e lunghezza di 500 - 8000 mm (Fig. 2);
  - * laminatoio per la produzione di lamiere da 3 - 50 mm di spessore, 1000 - 2000 di larghezza e con lunghezza fino a 8000 mm;

- per i laminati lunghi, prodotti presso ILVA-AOSTA di:
    - * laminatoio per tondi fino a ϕ 20 mm;
    - * laminatoio per vergella fino a ϕ 5.5 mm
- per la fabbricazione di tubi saldati si impiegano le linee di saldatura al plasma della Dalmine.

Le attività di messa a punto hanno riguardato la trasformazione di lingotti di Ticp ϕ 140 mm in barre da 35 mm eseguita mediante fucinatura con martellatrice ad Aosta per conto della Ginatta (Fig. 3), e il processo di trasformazione di bramme di Ticp in prodotti piani (coils a caldo e freddo e lamiere ricotte e decapate).

Nel caso dei prodotti piani, in particolare, si è lavorato sulla ottimizzazione delle fasi principali del processo (riscaldo, laminazione, decapaggio), e di quelle di condizionamento intermedio dei semilavorati, relative alla trasformazione di bramme da 150 a 300 mm in nastri a caldo e freddo per impieghi industriali.

In questo contesto è stato definito il ciclo per la fabbricazione di nastri sottili (< 1 mm di spessore), ciclo che è rappresentativo di un elevato standard qualitativo visto il controllo che si deve mantenere nelle varie fasi della trasformazione per evitare la formazione di difetti ed assicurare l'elevata qualità superficiale del prodotto finale.

In pratica è stato definito il processo per la produzione di nastri 0.7 X 99.3 mm in Ti Gr 2 destinati alla saldatura in tubi 1' 1/4" per condensatori ad acqua di mare per centrali di potenza.

Tale ciclo si può sintetizzare nelle seguenti fasi:

- riscaldo delle bramme (170 x 1030 x 4800 mm) in forni a $CH_4$ secondo un ciclo appositamente studiato evitando qualsiasi inquinamento con altri metalli;

- laminazione diretta delle bramme e nastri a caldo da 3.5 mm avvolti in rotoli;

- ricottura e decapaggio (in acido nitrofluoridrico) in continuo dei nastri;

- laminazione a freddo a spessore 0.7 mm con una singola riduzione in più passate;

- trattamenti finali di sgrassaggio, ricottura, decapaggio.

Sono stati ottenuti dei nastri conformi alla specifica Dalmine per la trasformazione in tubi per quanto concerne le caratteristiche meccaniche, dimensionali, di rugosità (Tab. 1).

I nastri sono stati saldati presso la Dalmine per fabbricare tubi 31.7 x 0.7 x 18500 mm che hanno, come si vede in Tab. 2, caratteristiche meccaniche conformi alla specifica ASTM B338 ed hanno ottenuto l'omologazione all'impiego da parte dell'ENEL che li utilizzerà in uno dei condensatori ad acqua di mare della centrale policombustibile di Brindisi.

Sui nastri impiegati dalla Dalmine per ricavare i tubi è stata effettuata anche un'indagine sulle caratteristiche superficiali che influenzano il comportamento del nastro durante la trasformazione a tubo.

A tale scopo sono stati sottoposti ad analisi chimica superficiale all'ESCA nastri trattati diversamente e con una rugosità confrontabile.

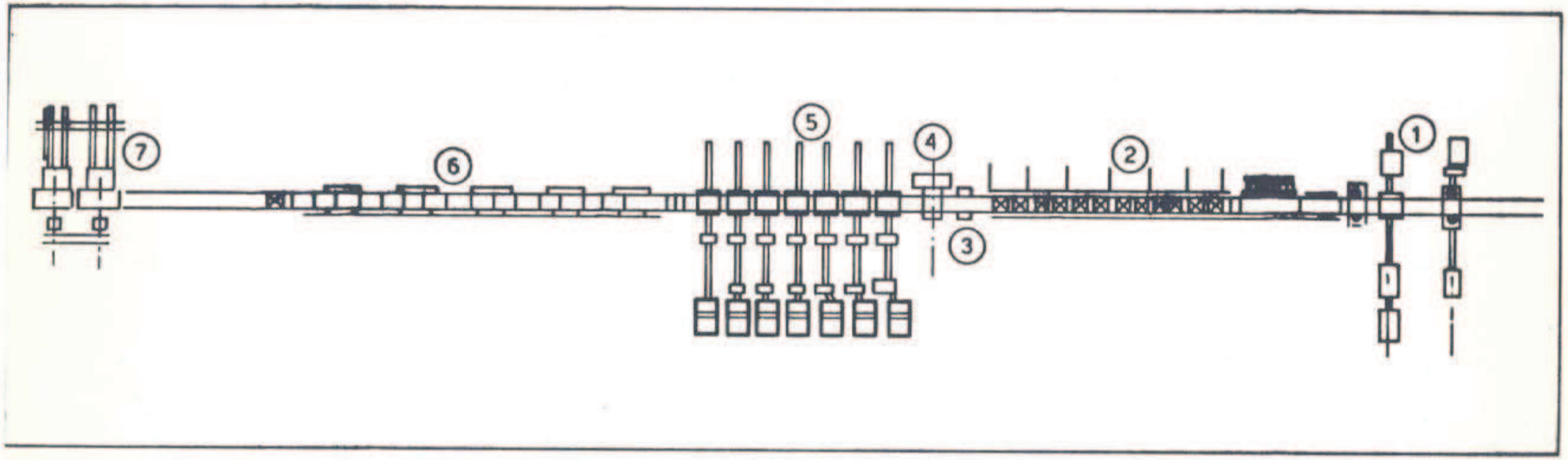
In pratica è stata determinata la composizione di uno strato superficiale del nastro sottoponendolo ad erosione all'ESCA per un tempo totale di ca. 130 min, che corrisponde ad una profondità dello strato analizzato di ca. 0.2 μm.

Sono state individuate due situazione diverse, fondamentalmente per quanto riguarda i contenuti di C e O nei primi strati superficiali (primi 30 - 40 min di erosione); i contenuti di C e O sono risultati variabili tra 10 - 60% At in un caso e tra 10 - 50% At nel secondo con un assestamento negli strati più interni su valori del 10% At sia per l'O che per il C nel primo caso e su livelli maggiori (25 - 30% At) nel secondo, che è risultato anche comportarsi meglio nella trasformazione a tubo (Fig. 4).

In conclusione sono state sintetizzate le caratteristiche principali degli impianti nella produzione di manufatti in Ticp con esempi di attività finalizzate alla messa a punto dei relativi cicli di lavorazione per prodotti per vari impieghi industriali.

Queste attività finalizzate di messa a punto prodotti e relative tecnologie di lavorazione proseguiranno e saranno ampliate con indagini nel campo della metallurgia fisica, delle proprietà di impiego e delle tecnologie di fusione e di trasformazione più recenti (E.B., plasma, superplasticità , ecc.) del Ti e sue leghe.

RD/gf(N39,C60299)



① **Sbozzatore**
② **Forno di mantenimento intermedio**
③ **Riscaldatore ad induzione per i bordi**
④ **Cesoia**
⑤ **Treno finitore**
⑥ **Piano di raffreddamento**
⑦ **Aspi**

Fig. 1 – Schema del laminatoio a caldo

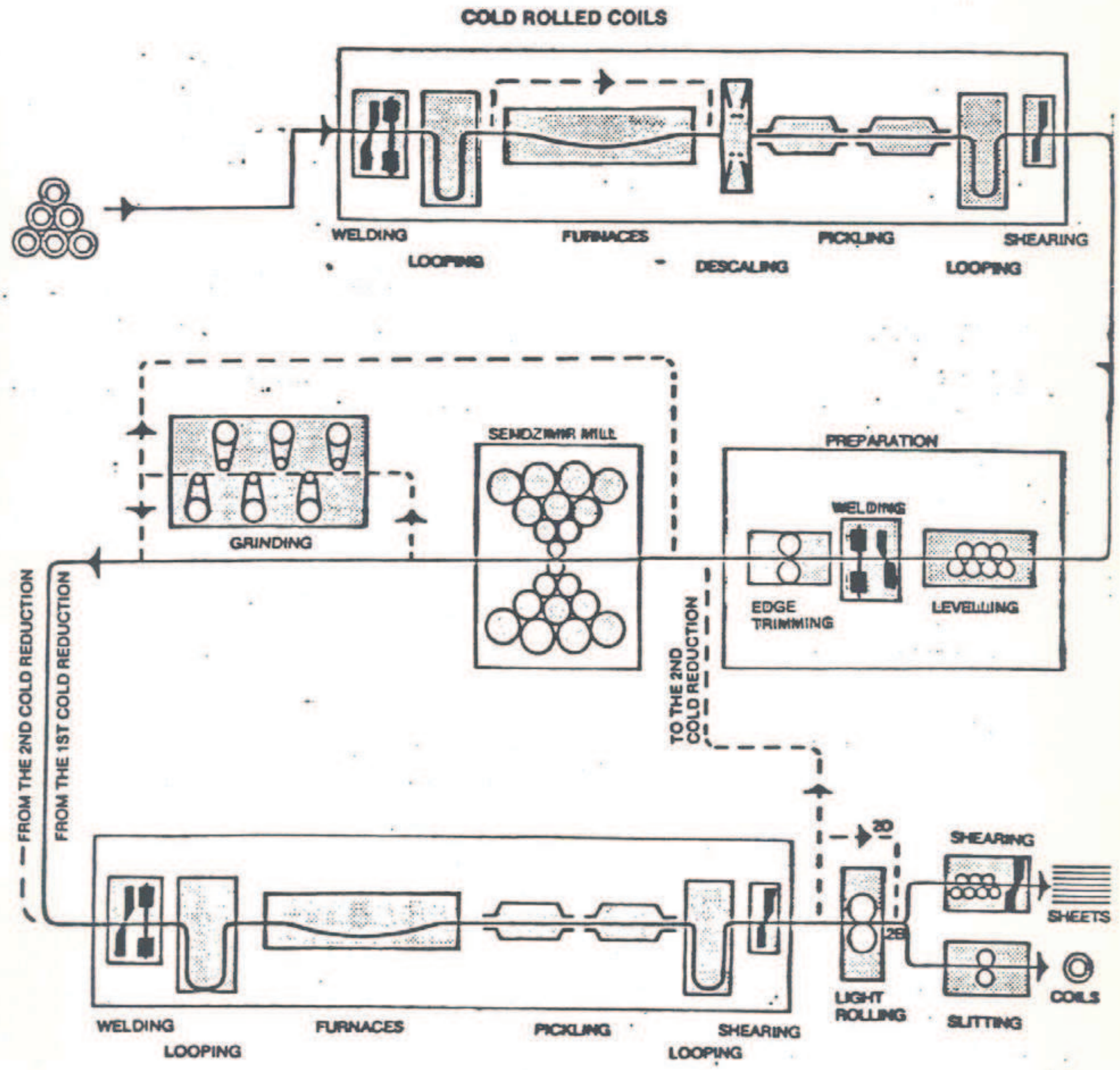


Fig. 2 - Schema del ciclo produttivo dei laminati a freddo in Ti
(linee di decapaggio e ricottura; laminatoio Sendzimir)

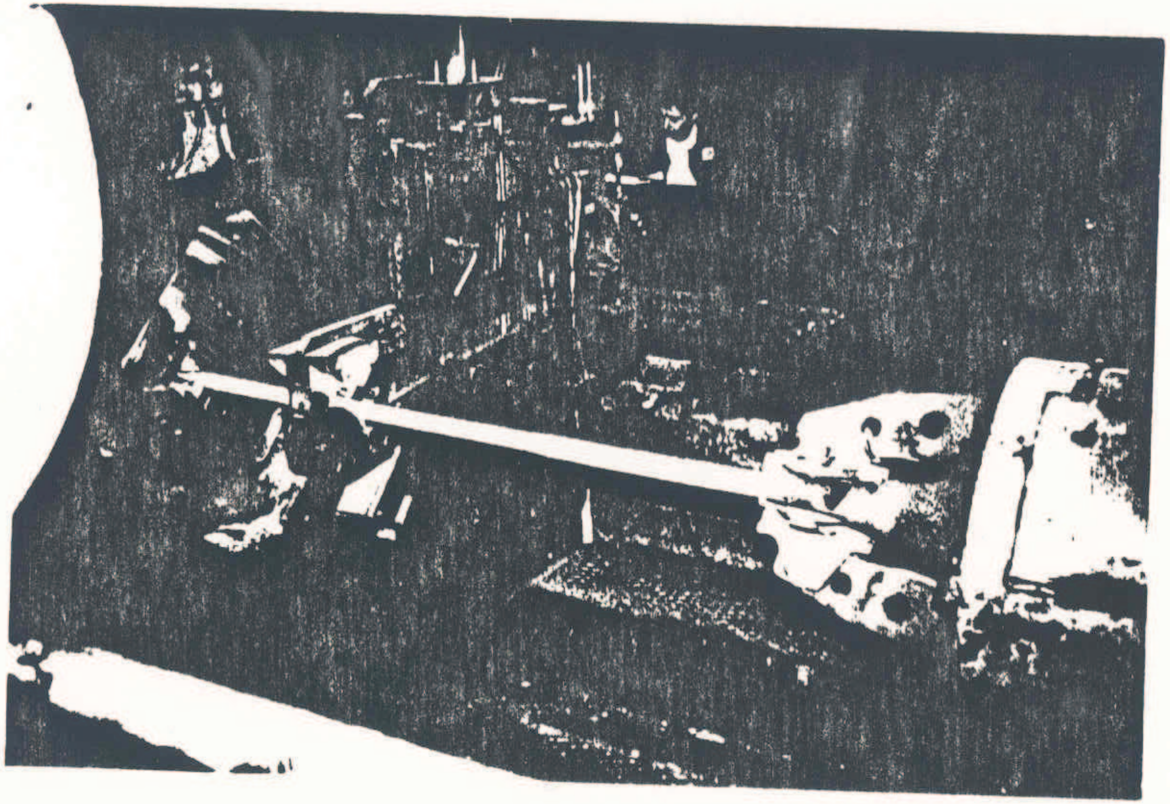


Fig. 3 - Fabbricazione di barre Ø 35mm mediante martellatrice

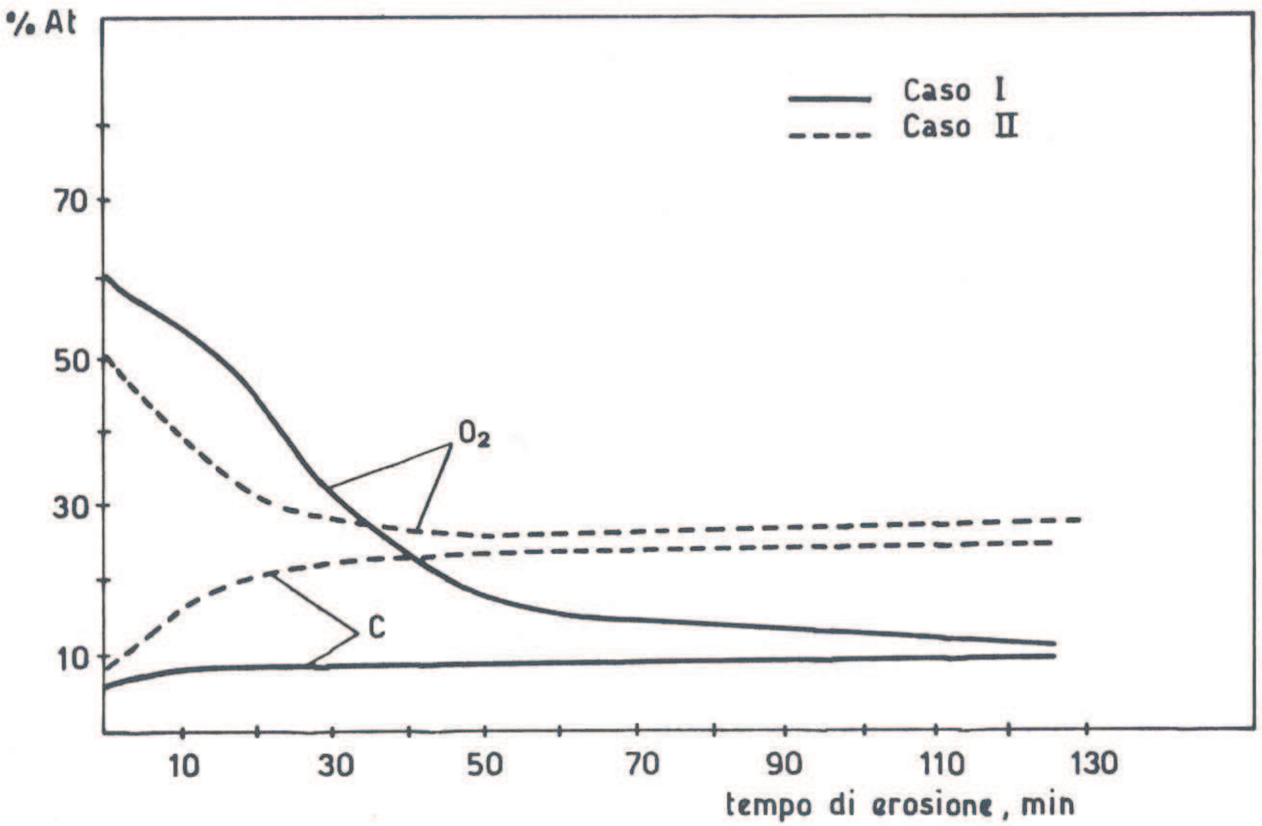


Fig. 4 - Andamento dei contenuti di C ed O negli strati superficiali dei nastri utilizzati dalla Dalmine per la fabbricazione di tubi per scambiatori di calore

|  | Rp 0.2 % N/mm² | Rm N/mm² | A % | Grandezza grano (ASTM E 112) | Rugosità Ra μm |
|---|---|---|---|---|---|
| RICHIESTO | 230 ÷ 330 | > 345 | > 24 | 6 ÷ 9.5 | ≤ 0.6 |
| OTTENUTO | 280 ÷ 320 | > 370 | > 26 | 7 ÷ 8 | 0.30 |

Tab.I – Caratteristiche meccaniche dei nastri da 0.7 mm .

| | SNERVAMENTO MPa | ROTTURA MPa | ALLUNGAMENTO % |
|---|---|---|---|
| RICHIESTO* | 275÷450 | ≥ 345 | ≥ 20 |
| OTTENUTO | 290÷305 | >380 | > 44 |

* Specifica ASTM B 338/83 ; ENEL 9x0-3614-SMTU-GM-01

Tab.II _ Caratteristiche meccaniche dei tubi fabbricati con i nastri ILVA _

# COMBUSTION SYNTHESIS OF TITANIUM-BASED SHAPE MEMORY INTERMETALLIC MATERIALS*

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## ABSTRACT

Ni-Ti-X (X=Fe,Pd) shape memory alloys (SMA) have been produced by combustion synthesis using the thermal explosion mode resulting in a liquid intermetallic product. The solidified products were subsequently hot rolled into plates exhibiting the shape memory effect (SME) with transition temperatures ranging between -78°C to 460°C by substituting nickel, in part or totally, with iron or palladium. The potential for producing intermetallic compounds using combustion synthesis is discussed from a thermodynamic standpoint. It is argued that the value of $\Delta H^\circ_{f,29}8/C_{p,298}$ may play a key role in this method of synthesis and fabrication for these materials.

## 1. INTRODUCTION

During the past two decades there has been increasing interest in shape memory alloys (SMA) since they are capable of "remembering" their original shape. Prominent applications have been proposed to exploit these unusual alloys such as in temperature sensing instruments used in automatic controllers[1].

There are three methods of producing SMA's as shown in Fig. 1. The conventional technique is by arc or induction furnace melting of the constituents, followed by casting and thermomechanical processing into the final products (Fig. 1a). The arc melted products need to be melted several times to achieve acceptable homogeneity, whereas for vacuum induction melting contamination by the graphite crucible is often inevitable. The cast alloys often display microstructural segregation which has to be removed by subsequent mechanical working or heat treatment. Until recently almost all of the SMA's were produced in this way.

The second method is by powder metallurgy (PM) techniques which offer the potential for near net shape processing with decreased microstructural segregation (Fig. 1b). The PM method has been used to produce NiTi[2,3] and Cu-Al-Ni[4] alloys. The well known major disadvantage of this technique is the need for a prolonged sintering time.

The third method of producing SMA's is by using self propagating high temperature synthesis (SHS) or combustion synthesis. SHS offers savings in time and energy since the processing time is on the order of seconds or minutes compared with hours or days in the conventional melting or PM methods (Fig. 1c). Originally, SHS was used to produce ceramic or composite materials which exhibit such exothermic characteristics that the reaction proceeds in a self-sustaining way.

There are two possible modes of combustion in SHS: the combustion mode and the thermal explosion mode. In the combustion mode the compacted powder reagents are ignited at one end of the specimen and the reaction front

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* to be published in Journal of Metals

proceeds in a self-sustaining manner through the specimen leaving the reacted product at the reaction front. In the thermal explosion mode the whole specimen is heated in a furnace until the reaction occours. Fig. 2 shows a typical exothermic peak for the combustion process where Tig is the ignition temperature, i.e. the temperature at which the reaction commences, and Tc is the combustion or maximum temperature attained in the specimen.

The combustion mode has been used to produce both NiTi[5,6] and Cu-based (Cu-Al-Ni and Cu-Al-Mn) SMA's[7]. Owing to the lower combustion temperature, the products were porous necessitating subsequent remelting[5,7] or hot-extruding[6] into the final alloy form with shape memory characteristics. On the other hand, Yi and Moore[8,9] found that the thermal explosion mode offers a much improved product for producing NiTi alloys. In the latter case, the combustion temperature was higher than the melting point of the SMA and a liquid product was obtained. It has been demonstrated that the cast product can be readily fabricated into the final required form possessing shape memory characteristics.

## 2. THE SHAPE MEMORY EFFECT (SME) AND SHAPE MEMORY ALLOYS (SMA)

Bending a shape memory alloy at a temperature below its transition temperature followed by heating above the transition temperature results in complete recovery of the SMA to its original shape. This is due to the reversible change between its martensitic phase and its parent phase. Typically, strains of 6-8% can be completely recovered.

Many alloys which exhibit a thermoelastic martensitic transformation have been found to exhibit SME characteristics including NiTi-X series, Cu-based series (mainly Cu-Zn-Al and Cu-Al-Ni), Fe-based (e.g. Fe-Pt and Fe-Ni-Co-Ti) series and precious metal series (e.g. AuCd and AuZn). Each of these alloy systems have a very small (Ms-As) transformation hysteresis and their martensitic microstructures contain twins instead of dislocations or stacking faults. These are believed to be the prerequisites to the SME. Until now, the commercially available SMA's have been based on the Ni-Ti, Cu-Zn-Al and Cu-Al-Ni series. The latter two are cheaper than Ni-Ti, but Ni-Ti possesses superior mechanical properties and good resistance to erosion. Unfortunately, the transition temperatures for all of these SMA's are usually between room temperature and slightly over 100°C. For instance, the previously reported transition temperatures for binary Ni-Ti alloys are usually between 30°C[10] and 115°C[11]. For Cu-Al-Ni, the highest reported transition temperature (Ms) is 155°C, produced by sintering the pre-alloyed powders[4].

In order to extend the applications of these alloys it is necessary to extend their transition temperatures over as wide a temperature range as possible. Adding a third element is one possible avenue of investigation. For instance, in the Ni-Ti SMA's, substituting Ti with Zr or Ni with Au can increase the transition temperatures whereas substituting Ni with Fe or Co decreases the transition temperature[11].

Donkersloot and Van Vucht[12] showed the transition temperature for TiPd to be 510°C, for TiAu, 620°C and for TiPt, 1070°C. Therefore, it is expected that substituting Ni with Au, Pd or Pt should increase the transition temperature. Khachin et al[13] subsequently showed that by the addition of more than 20 at% Pd as a substitute for Ni greatly increased the transition temperatures, and a successfully fabricated SMA with 20-35 at% Pd was obtained by Tuominon and Biermann[14].

All of these alloys were produced by the conventional melting/casting procedure. However, Yi and Moore have recently successfully produced Ni-Ti[8,9] and Ni-Ti-Fe, Ni-Ti-Pd[15] SMA's with a wide variation in transition temperatures using the SHS method. The characteristics of this method and its potential for producing other intermetallic-based SMA's is discussed in this paper from a thermodynamic point of view.

## 3. PRODUCING INTERMETALLIC BASED SMA'S USING THE THERMAL EXPLOSION MODE OF SHS

Since, in the thermal explosion mode of SHS, the whole pellet is heated in a furnace, it is more effective in providing an adiabatic reaction process than that of the combustion mode in which heat dispersion from the specimen is inevitable. Fig. 3 shows the relationship between enthalpy and temperature for both reactants and product. At the ignition temperature, Tig, the synthesis reaction is initiated. If the process is adiabatic the whole heat of formation is consumed in heating the sample to the combustion temperature, Tc, i.e. $\Delta H_{f,Tc}$ is zero.

Since

$$\Delta H_{f,Tc} = \Delta H_{f,Tc} + {}_{Tig}\int^{Tc} Cp(T)dT = 0$$

thus

$$-\Delta H_{f,Tig} = {}_{Tig}\int^{Tc} Cp(T)dT \qquad (1)$$

Where Cp is the heat capacity of the product. Since, the combustion temperature depends on the value of $\Delta H_{f,Tig}$ and Cp, the ratio of $\Delta H_{f,Tig}/Cp$ should be a measure of the combustion temperature. If the combustion is sufficiently exothermic that its combustion temperature is higher than the melting point of the product, the reacted pellet will be in the liquid state enabling a cast alloy to be obtained. In this case the latent heat of fusion needs to be incorporated into equation (1). On the other hand, for conditions in which the combustion temperature is less than the melting point of the product, the reaction may not be complete resulting in a porous product and subsequent compaction and sintering treatments are necessary.

Table 1 gives the standard heats of formation, $\Delta H^\circ_f$, and heat capacities, Cp, at 298K for some of the intermetallic SMA's. Ignition and combustion temperatures are also listed where possible. All of the pellets were compacted in the present investigation to an initial green density of approximately 67% of theoretical. From Table 1 it can be seen that the Cp values are not greatly different for these compounds indicating a greater dependence on the more variable $\Delta H^\circ_{f,298}$ values in order to achieve the higher combustion temperatures.

Since

$$\Delta H^\circ_{f,298}(TiFe) < \Delta H^\circ_{f,298}(NiTi) < \Delta H^\circ_{f,298}(TiPd) \qquad (2a)$$

then

$$Tc(Ti+Fe\rightarrow TiFe) < Tc(Ti+Ni\rightarrow TiNi) < Tc(Ti+Pd\rightarrow TiPd) \qquad (2b)$$

providing the combustion is adiabatic (eq. 1).

This trend is consistent with the experimental data shown in Table 1. For instance, the $\Delta H^\circ_{f,298}$ value of TiPd is -24.7 kcal $mol^{-1}$ and its combustion temperature is greater than 1873 K which is more than 200 K higher than its melting point. On the other hand TiFe with a $\Delta H^{\circ}_{f,298}$ of -9.7 kcal $mol^{-1}$ provides a combustion temperature lower than its melting point. It appears, therefore, that in order to obtain a cast product the synthesised compounds need a sufficiently high ratio of $\Delta H^{\circ}_{f,298}/Cp_{,298}$. Evidence to support this assumption is that the $\Delta H^{\circ}_{f,298}$ values for most non-intermetallic solid solution alloys are lower than that of intermetallic alloys. For such alloys, the combustion temperatures are lower than their melting points, as in the case of combustion synthesis of Cu-based SMA's[7] and Cu-Al binary alloys[22]. TiFe is the only compound in Table 1 which follows the latter trend, i.e., the Tc is less than the melting point. This paper is largely concerned with NiTi and TiPd intermetallics with $\Delta H^{\circ}_{f,298}/Cp$ values of 1423K and 2020K respectively. Therefore, liquid products should be readily achieved under adiabatic processing conditions in these two systems.

According to eq. 2 and assuming that the heat of formation for solid solution can be neglected compared with that of formation of the intermetallics, it can be stated that:

$$\Delta H^{\circ}_{f,298}(TiFe) < \Delta H^{\circ}_{f,298}(NiTiFe) < \Delta H^{\circ}_{f,298}(NiTi)$$

and

$$\Delta H^{\circ}_{f,298}(NiTi) < \Delta H^{\circ}_{f,298}(NiTiPd) < \Delta H^{\circ}_{f,298}(TiPd)$$

This indicates that, compared with the combustion synthesis of $Ni+Ti \rightarrow NiTi$ reaction, the substitution of Ni with Fe should decrease the combustion temperature, and the substitution of Ni with Fe should increase the combustion temperature. In each case, a liquid product is expected and the following reactions should result:

$$Ti(s) + Ni_{0.5-x}(s) + xFe(s) \rightarrow TiNi_{0.5-x}Fe_x(l);\ x \leq 0.1 \qquad (3a)$$

$$Ti(s) + Ni_{0.5-x}(s) + xPd(s) \rightarrow TiNi_{0.5-x}Pd_x(l);\ 0.23 \leq x \leq 0.5 \qquad (3b)$$

where s denotes solid and l denotes liquid respectively. The value of x in eq. (3) is the stoichiometric range used in the present investigation.

## 4. EXPERIMENTAL METHOD

The powders used for this investigation were purchased from Goodfellow Company, England. Their particle sizes and purities are listed in Table 2.

The powders were mixed in the required stoichiometry and subsequently tumbled thoroughly to achieve homogeneity before being pressed, in air, into pellets using a two plunger die system. Each pellet weighed approximately 1.5g with a density of 67±2% of theoretical. A hole was drilled at one end of the pellet to accommodate the Pt-Pt/Rh thermocouple which was used together with a linear chart recorder to measure temperature changes during heating. The pellets were reacted in a tube furnace under a flowing argon atmosphere.

Iron was chosen to substitute, in part, for nickel in order to decrease the transition temperatures whereas palladium was chosen as the candidate to replace nickel in order to increase the transition temperature. For the $TiNi_{0.5-x}Pd_x$ series of alloys, as the heat of formation of TiPd is more negative than that of NiTi as shown in Table 1 and, therefore, should result in a liquid product. Using similar reasoning the $TiNi_{0.5-x}Fe_x$ products can also be obtained in the cast state provided the iron addition is not too large.

The reaction time was typically less than one second although approximately one minute was usually needed to heat the sample to its ignition temperature. It was found that all of the reacted products provided a combustion temperature greater than their melting points so that the products were in a liquid state immediately after the reaction. The samples were subsequently cooled in flowing argon and hot rolled into plates at approximately 800°C with a thickness of about 0.5mm. They were then shape memory annealed at 600°C for 2 hours followed by air cooling. The products were found to exhibit shape recovery during the hot-rolling process.

Transition temperatures were determined by either electrical resistance (ER) measurements or by differential thermal analysis (DTA) using a heating rate of 10°C/min.

## 5. RESULTS AND DISCUSSION

### 5.1 Combustion Synthesis of Ni-Ti

The reaction between Ni and Ti was found to be sufficiently exothermic that its combustion temperature (Tc) was 1773K, more than 260K higher than the melting point of NiTi. It was also found that both the heating rate and nickel particle size had little effect on Tc and Tig for this alloy series[9].

The cast product was very readily hot rolled into plates which were found to exhibit the SME during the hot-working process. The microstructures were found to be sensitive to both the cooling rate from the liquid product and to the Ni particle size as shown in Fig.4. The product microstructure revealed the NiTi parent phase and a $NiTi_2$ second phase. The second phase exhibited a faceted shape on using a lower cooling rate and a dendritic shape with a higher cooling rate. The faceted $NiTi_2$ was believed to be responsible for a decrease in ductility of the product.

Transition temperatures were between 40-80°C which is consistent with published work. However, transition temperatures decreased with increase in Ni particle size[23]. This is because more $NiTi_2$ was formed (Fig.4) which resulted in a slight decrease in Ti content in the parent NiTi phase. The transition temperature decreases sharply as the Ti content in the parent NiTi phase deviates from equiatomic stoichiometry".

### 5.2 Combustion Synthesis of Ni-Ti-Fe

From the earlier discussion the value of $\Delta H^\circ_{f,298}$ is expected to decrease for the Ti-Ni-Fe ternary compounds. This will' result in a decrease of the combustion temperature on the stipulation that the combustion is an adiabatic process as shown in equation 1. However, it was found that eq 3a is true for x up to 0.1, since a liquid product was found in each case. This may be explained in that, since the substitution of Ni by Fe was less than 10 at%, this did not lower the $\Delta H^\circ_{f,298}/Cp_{,298}$ ratio sufficiently so that the Tc values were high enough to obtain a liquid product. Microstructural observations indicated that there was a large volume of second phase material formed apart from the shape memory parent phase. However, the ductility of the alloys was still very high suggesting a ductile second phase.

Table 3 shows the effect of substituting Fe for Ni on the combustion characteristics and transition temperatures. Since the substitution of Ni with Fe does not greatly change $\Delta H^\circ_{f,298}$(NiTiFe) the experimental values of Tig and Tc were not greatly changed. As shown in Table 3, this has proved to be a satisfactory approach in that the transition temperatures decreased dramatically on increasing the substitution of Ni with Fe up to 10 at%. This is consistent with published results using conventional melting and thermomechanical techniques far producing these alloys.

## 5.3 Combustion Synthesis of Ti-Ni-Pd

Table 4 shows the effect of substituting Pd for Ni on the heat of formation and combustion characteristics. It was found that eq.3b is also true far the compositions concerned in this investigation, i.e. for x between 0.23 and 0.5. Moreover, the reactions were actually completed in an explosive manner, as these reactions are far more exothermic than those of 3a. It is then suspected that the combustion temperatures should be far higher than those listed in Table 4. Since no attempts were made to accurately measure the Tc values in each reaction, the results listed in Table 4 should be treated as an approximation only. In some instances the thermocouples melted and/or broke immediately after the reaction took place.

Tuominen and Biermann[14] produced Ti-Ni-Pd SMA's with palladium contents up to 35 at% which exhibited Ms temperatures up to around 200°C. However, they were not successful in producing higher shape memory transition temperatures with higher Pd contents. They suggested that the reasons far this may be that the processing required for these alloys could differ significantly from that required for alloys containing less palladium. The current investigation, however, has established that all of the compounds listed in Table 4 exhibited the shape memory effect including $Ti_{50}Pd_{50}$. However, it appears that the recoverable strain is smaller in this latter alloy than the binary Ni-Ti series. The transition temperatures for each of the compounds are also listed in Table 4. It can be seen that the transition temperatures can indeed be greatly elevated by the addition of palladium. Fig. 5 summarizes the effect of substitution of Ni by Fe or Pd on the transition temperatures.

A typical microstructure is shown in Fig. 6. Using EDAX analysis on the SEM the dark phase was identified as $(Pd,Ni)Ti_2$. EDAX results also showed that the parent phase contained more Pd than that for an ideal solution, whereas an excess of Ni was found in the second phase. This indicates that the bonding capacity with titanium is different for the two elements in the two phases. Also, a deformed dark phase is apparent in Figure 6, indicating this phase is reasonably ductile.

The present investigation shows the Ms temperature for TiPd compound to be 459°C which is 51°C lower than that determined by Donkersloot et $al_{12}$. This is probably due to an increased amount of second phase being formed in the present investigation.

It is interesting to compare the ER curves among Ni-Ti, Ni-Ti-Fe and Ti-Ni-Pd SMA's as shown in Fig.7. The different ER curves reflect different transformation mechanisms. For NiTi SMA, the abnormal increase upon cooling corresponds to an intermediate rhombohedral R-phase formation prior to transforming into a distorted $B_{19}$ type structure. By substituting nickel with iron, this martensitic transformation can be retained to lower temperatures. In the case of Ti-Ni-Pd, there is no R-phase transition at all and the martensite is an orthorhombic $B_{19}$ structure.

A theoretical explanation for the effect of addition of a third element on the Ni-Ti martensitic transition is still not clear. Titanium, nickel, iron and palladium are all transition metals. For such alloys, there is a large charge transfer phenomenon upon alloying. The transition mechanism of such alloys must be closely related to the bonding mechanism and further research should pursue this area of investigation. However, some observations and comments may be worth discussing here.

A number of investigators have studied the effect of ternary alloying additions on the martensitic transformation in intermetallic compounds having $B_2$ structures. Previous researchers have invoked arguments based on such factors as atomic size, ionic size or electrochemical effects in an attempt at explanation. For instance Wang[24] noticed that transformation temperatures are related to the valence electron concentrations for some CsCl type compounds. Unfortunately, as indicated by Eckelmeyer[11], those explanations based on one particular factor are not successful in that they may only explain one type of alloy but not others. This led the present authors to consider a "mixing factor". The starting point is that the transformation temperatures must be closely related to the bonding energy of the alloys, whereas the bonding energy is closely correlated with atomic sizes, electron transfer effect upon alloying and electronegativities of the compounds. If the two elements in the binary alloy are both transition metals, Miedema et al[18] found that these factors have a simple relationship with the heat of formation of such compounds. The $\Delta H^\circ_f$ values estimated by this semi-empirical model was found to be highly consistent with the experimental values. From this it was assumed that the transformation temperatures may also be closely related to the $\Delta H^\circ_f$ values of such intermetallic compounds.

Fig. 8 shows the plot of the logarithm of Ms versus the $\Delta H^\circ_{f,298}$ for some compounds having $B_2$ structures. Although no simple relationship exists, there is a clear trend that the higher the $\Delta H^\circ_{f,298}$ value, the higher the transformation temperature. The TiFe compound has the lowest transformation temperature. This concept may be used to explain the effect of the addition of a third transition metal on the transformation temperatures of Ni-Ti SMA's. If the substitution of the third element lowers the $\Delta H^\circ_f$, the transformation temperature will be decreased. This is the case using Fe or Co to substitute for Ni since both $\Delta H^\circ_{f,298}$(TiFe) and $\Delta H^\circ_{f,298}$(TiCo) are lower than that of NiTi. On the contrary, substituting Ti with Zr or Ni with Au, Pd or Pt can increase the transformation temperatures since the overall $\Delta H^\circ_{f,298}$(Ni-Ti-X) values are increased. This can also be seen in Figure 5.

It should be pointed out that this concept appears to apply best to two transition metals forming intermetallic compounds. For transition-nontransition alloys such as Au-Cd, Au-Zn etc. the rule does not work well. The bonding mechanisms for these latter alloys are not well understood, and Miedema's theory does not provide a satisfactory answer either. Also the concept suggested above does not explain why less than 20 at% Pd substitution for Ni lowers the transformation temperature. In this respect, the results shown in Figure 5 are in general agreement with Khachin et al[13]. It is hoped that the above suggestions to explain this effect may bring more discussion to this interesting phenomenon.

## 6. CONCLUSIONS

Combustion synthesis is a new and promising method of producing Ni-Ti series shape memory alloys. It has the advantage of both time and energy savings compared with the conventional melting or powder metallurgy approaches. The $\Delta H^\circ_{f,298}/C_{p,298}$ value plays a key role in this method, especially if a liquid product is required.

Shape memory transition temperatures can be tailored aver a wide temperature range by the substitution of Ni for a third element such as Pd or Fe. This approach should greatly extend the application of such alloys.

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Table 1. Relationship Between Heats of Formation and Combustion Temperatures

| Compounds | $\Delta H^\circ_{f,298}$ kJmol$^{-1}$ | $C_{p,298}$ Jmol$^{-1}$K$^{-1}$ | $\Delta H^\circ_{f,298}/C_{p,298}$ K | Tig K | Tc K | Tmp K |
|---|---|---|---|---|---|---|
| TiNi | -66.5 (16) | 46.8 (16) | 1423 | 1183+ | 1773+ | 1513 |
| TiPd | -103.4 (17) | 51,2* | 2020 | 273(21) | >1873(21) | -1663 |
| TiPt | -159.5 (17) | 51.2* | 3120 | - | - | 2106 |
| NiAl | -118.4 (16) | 45.9 (16) | 2577 | - | 1923 (19) | 1912 |
| TiAl | -72.8 (16) | 49.3 (16) | 1478 | - 993+ | 1734+ | 1733 |
| TiFe | -40.6 (16) | 49.3 (16) | 868 | - | 1423 (20) | 1590 |
| TiCo | -47.7 (18) | 50.1* | 936 | - | 1723 (21) | 1610 |

*Estimated by Neumann-Kopp's rule
() Reference for calculations
+Present experimental results

Table 2. Powders used in Present Work

| Elements | Ti | Ni | Pd | Fe |
|---|---|---|---|---|
| Particle Size, $\mu m$ | <44 | <63 | 45-400 | <44 |
| Purity, % | <0.5 | <0.01 | <0.05 | - |

Table 3. Effect of Iron Substitution for Ni on the Combustion Parameters and Transformation Temperatures* of NiTi Compounds

| Compounds | Density, % theoretical | $-\Delta H^\circ_{f,298}$ kJ mol$^{-1}$ | Tig°C | Tc°C | Tp°C | Ms°C |
|---|---|---|---|---|---|---|
| TiNi | - | 66.5 | 923 | 1500 | 70 | 15 |
| TiNi | 67.0 | 66.5 | 910 | 1480 | 82 | 39 |
| $TiNi_{47}Fe_3$ | 68.6 | 64.9 | 915 | 1362 | 35 | -65 |
| $TiNi_{45}Fe_5$ | 66.4 | 63.9 | 892 | 1510 | -40 | - |
| $TiNi_{44}Fe_6$ | 66.4 | 63.4 | 853 | 1369 | -78 | - |
| $TiNi_{43}Fe_7$ | 68.2 | 62.9 | 900 | 1362 | <-140 | - |
| $TiNi_{40}Fe_{10}$ | 67.3 | 61.3 | 908 | 1348 | - | - |

*Transformation temperatures measured by electrical resistance (ER). Tp - incommensurate phase start temperature. Ms - martensite start temperature

Table 4. Combustion Parameters and Transformation Temperatures of the Ti-Ni-Pd Compounds Synthesised by the SHS Method

| Sample | Compounds | Density, % theoretical | $-\Delta H_{f,298}$, kJ mol$^{-1}$ | Tig °C | Tc °C | Ms °C | Mf °C | As °C | Af °C |
|---|---|---|---|---|---|---|---|---|---|
| 1 | $Ti_{50}Pd_{50}$ | 69.7 | 102 | 1000 | >1600 | 459 | 427 | 497 | 533 |
| 2 | $TiNi_{10}Pd_{40}$ | 68.4 | 94.9 | 860 | 1285 | 321 | 287 | 327 | 366 |
| 3 | $TiNi_{20}Pd_{30}$ | 71.9 | 87.8 | 853 | 1320 | 108 | 80 | 109 | 153 |
| 4 | $TiNi_{22}Pd_{28}$ | 72.5 | 86.4 | - | 1447 | - | - | 132 | 180 |
| 5* | $TiNi_{27}Pd_{23}$ | 68.2 | 87.8 | 860 | 1350 | 50 | 25 | 45 | 85 |

*Transformation temperatures measured by electrical resistance (ER), others by differential thermal analysis (DTA) Ms, Mf, As, Af - martensite start and finish, austenite start and finish, respectively.

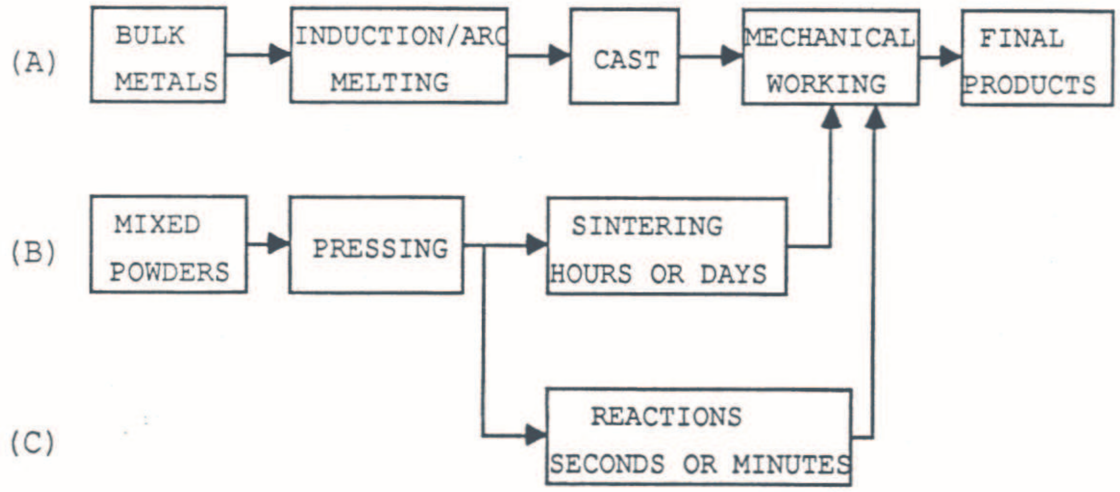

Figure 1. Schematic representation of three methods of producing SMA's: (a) Conventional melting; (b) powder metallurgy; (c) Combustion synthesis

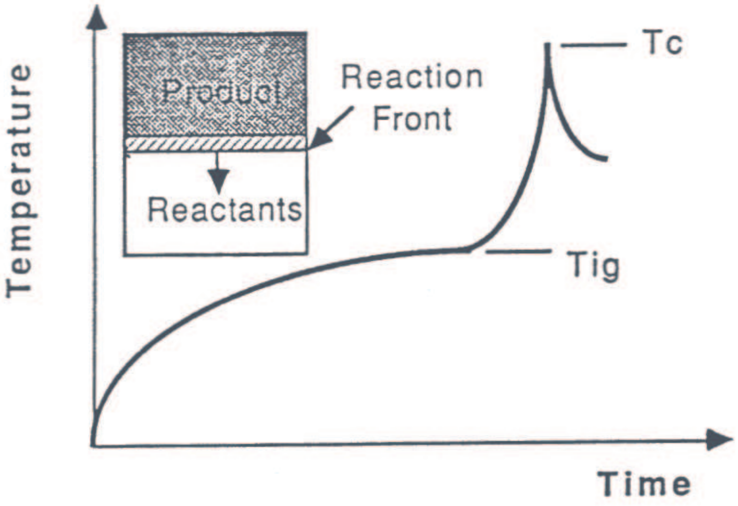

Figure 2. Schematic representation of the combustion process.

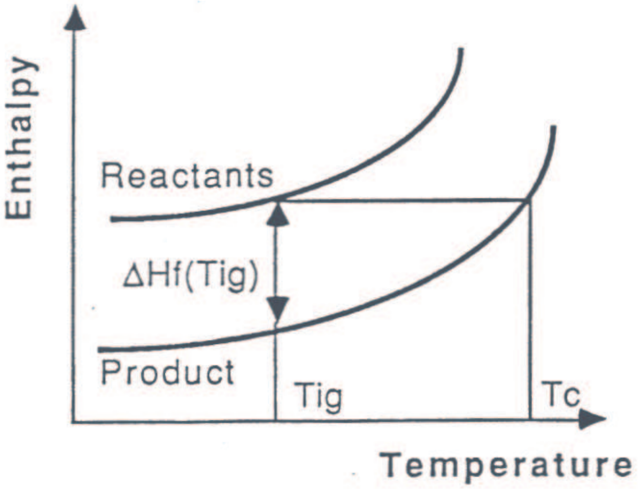

Figure 3. Enthalpy-temperature plot for an adiabatic combustion process.

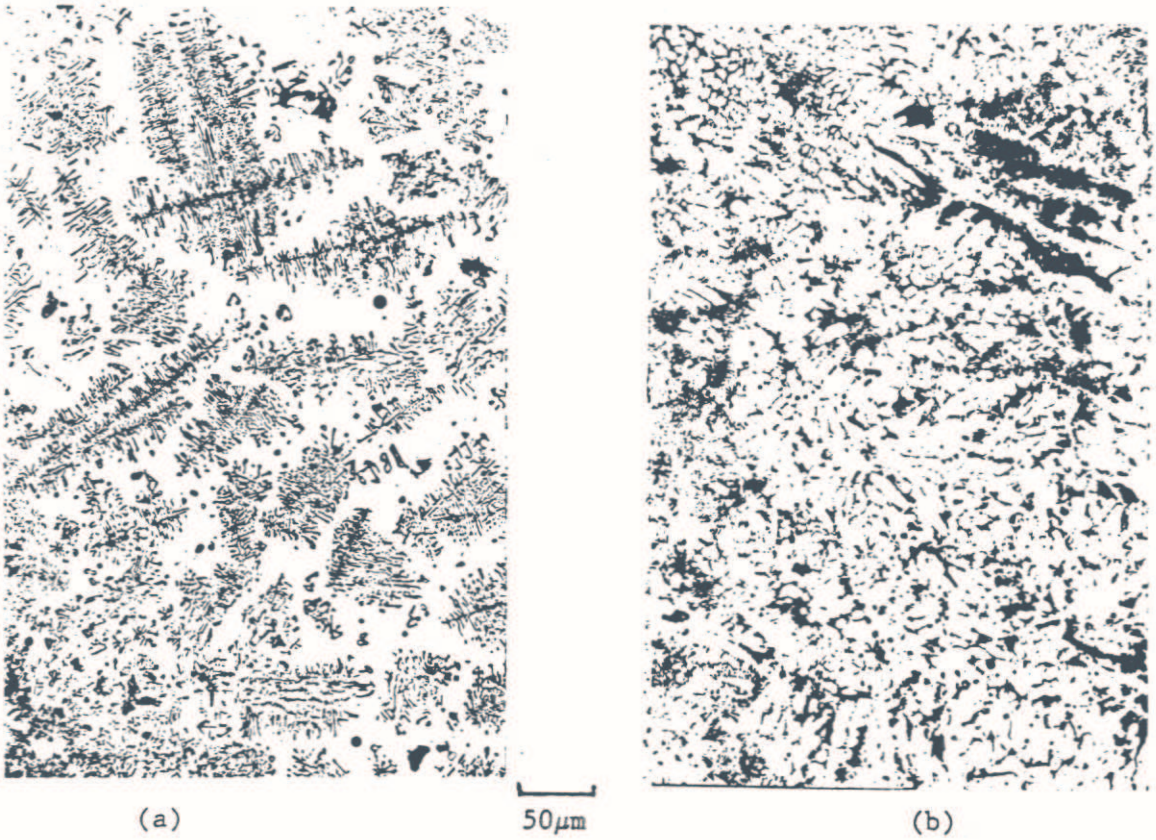

Figure 4. Typical microstructure of NiTi Synthesised with (a) 63-90 μm Ni powder and (b) 10-20 μm Ni powder

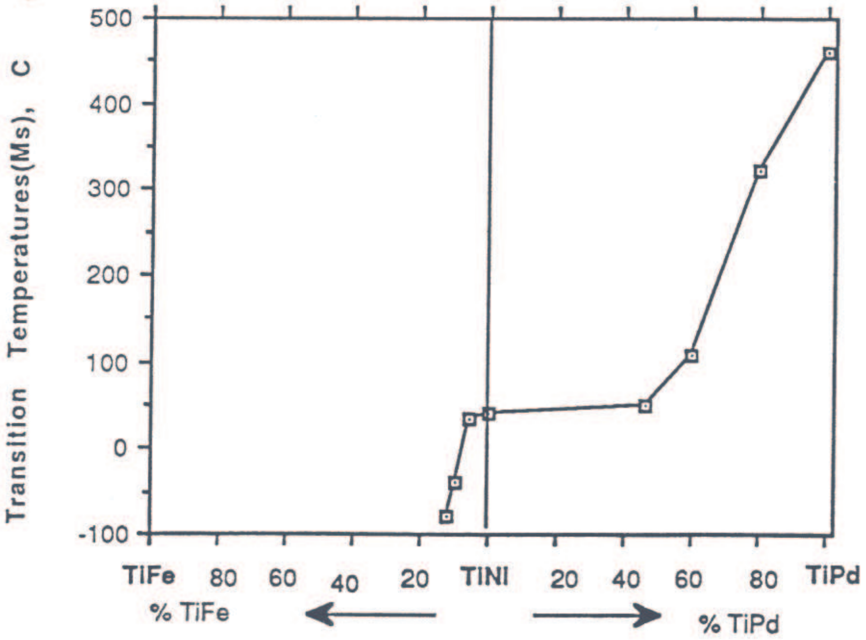

Figure 5. Effect of substitution of Ni by Pd or Fe on the Ms Transformation temperature of the ternary intermetallics.

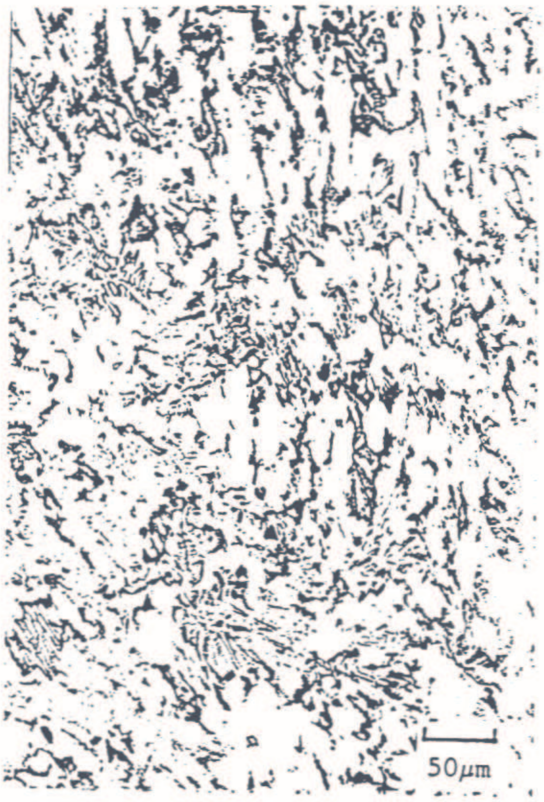

Figure 6. Typical photomicrograph for (a) $Ti_{50}Ni_{10}Pd_{40}$ - sample 2. The dark phase is $(Pd,Ni)Ti_2$

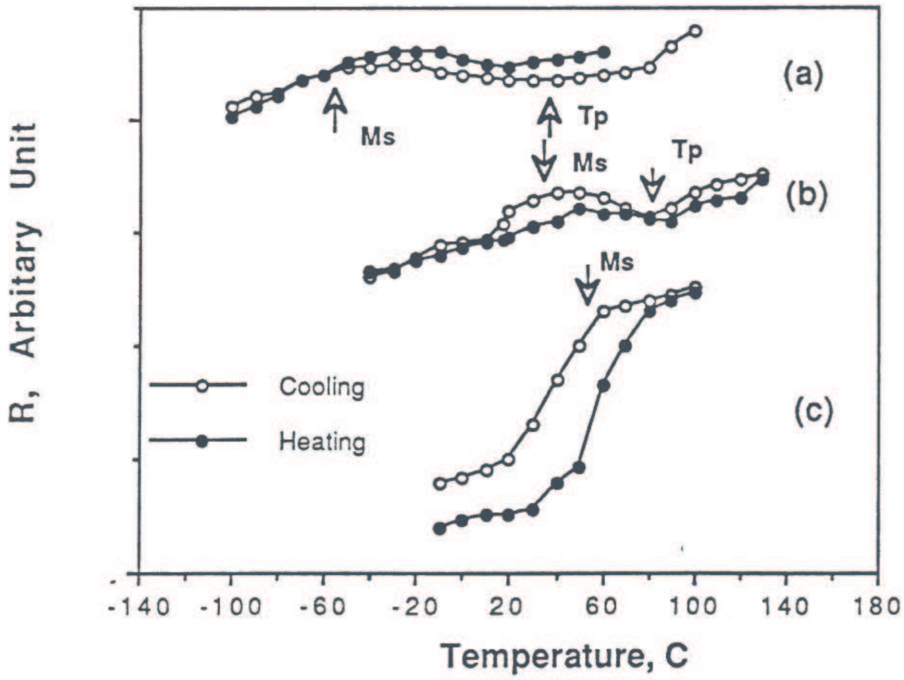

Figure 7. Electrical resistance (ER) - temperature plots for (a) NiTiFe, (b) NiTi, (c) NiTiPd intermetallics.

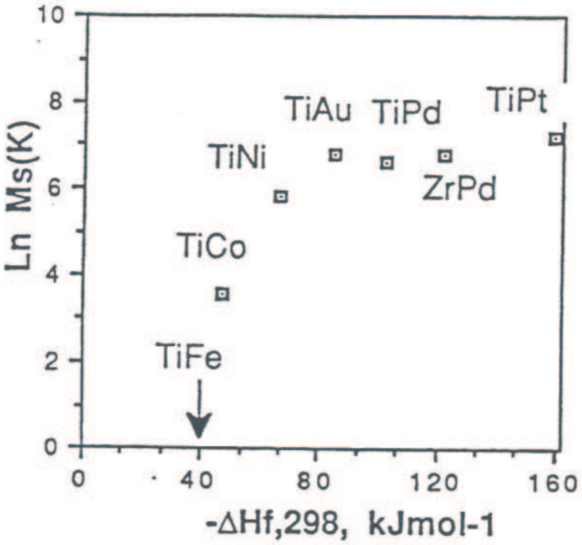

Figure 8. Effect of heat of formation at 298K on the Ms transformation temperature for selected compounds with $B_2$ type structures.

Raffaele Angelini, Bonetti S.p.A.

# UNA APPLICAZIONE DEL TITANIO SU GALLEGGIANTI AD ALTA PRESSIONE E TEMPERATURA.

L'applicazione che intendiamo descrivere riguarda la soluzione di un problema noto solo a pochi “addetti ai lavori”, e tuttavia ci sembra che valga la pena di parlarne per il motivo che, conti alla mano come vedremo, senza il Titanio ASTM B265 Gr. 4 il problema sarebbe ancora irrisolto.

Per questa applicazione l’elemento “tecnologico” è un galleggiante, (brevettato dalla C. BONETTI S.p.A.) che deve operare con:

. pressioni esterne fino a 210 bar
. temperature fino a 380°C
. densità relativa del liquido poco maggiore di 0,5

Diciamo subito che galleggianti per queste condizioni sono ancora fattibili, ma esistono altri possibili “stati” quali:

. pressione esterna 220 bar
. temperatura 30°C
. densità relativa 1

oppure:
. pressione esterna, qualche decina di bar
. temperatura 300°C
. densità circa 0,9

E inoltre, passaggi da una condizione all'altra in modo rapido e casuale.

L'inviluppo delle condizioni è quindi tale che gli accorgimenti buoni per un caso, sono forse negativi per un altro: ad esempio un liquido evaporante nell'interno del galleggiante, con l'aumento della temperatura dà luogo a una pressione interna che tende a bilanciare la pressione esterna e a compensare così anche la riduzione delle caratteristiche meccaniche del materiale dovuta alla temperatura: ma se la temperatura scende e la pressione cresce anche di poco, il galleggiante collassa.

Per descrivere la soluzione offerta dall'impiego del titanio non è necessario ripercorrere l'intera progettazione di questo sigaro leggero e resistente, e tanto meno ripassare tutte le verifiche di stabilità; basterà dare un'occhiata ai "passaggi chiave".

Intanto la forma ottimale è risultata quella di un cilindro a parete sottile con centine, dove centine e parete fanno corpo unico.

Il tutto come da disegno 1 e particolare A

I parametri geometrici di questa struttura sono parecchi, ma dopo aver imposto condizioni pratiche e relazioni teoriche i gradi di libertà si riducono a pochi.

Il parametro praticamente imposto dagli standard dei tubi, è il diametro D, nel nostro caso di 56 mm.

Per circa 200 bar a freddo (e ancora sempre in base alle disponibilità commerciali) lo spessore s è 0,8 mm. come verificheremo.

Consideriamo l'equazione (curva disegnata in fig. 2) :

$$\frac{M_x}{M_0} = e^{-\beta x}\left(sen\beta x + \cos\beta x\right)$$

con $\beta = \frac{\sqrt[4]{3\left(1-\nu^2\right)}}{rs}$ e $\nu = 0{,}33$, cioè $\beta = \frac{1.8}{\sqrt{Ds}}$

relativa all'influenza della centina, e imponiamo per la mezzeria (x=l) un valore prossimo allo zero (cioè contribuzione nulla). Dal diagramma ricaviamo

$$\frac{l}{\sqrt{Ds}} = 1{,}3$$

cioè $2l = 18mm$ .

Il momento d'inerzia della sezione del rinforzo più la parte del cilindro collaborante deve essere

$$J > K\frac{p}{24E}L_r D^3$$

dove $L_r = 4\sqrt{Ds}$ (e comunque $L_r \leq 2l$

e K è un fattore di sicurezza, per noi uguale a 1,5

cioè $J > 0{,}06 \cdot \frac{2}{10500} \cdot 18 \cdot 56^3 = 38mm^4$

La sezione resistente è un "T" costituito dalla sezione dell'anello e due ali ciascuna di spessore s (cilindro) e di estensione $0{,}55\sqrt{Ds} = 3{,}7mm$ il cui momento di inerzia è 40 mm$^4$.

Verifichiamo ora la stabilità a freddo in queste condizioni:

Dalla formula

$$p_c = \frac{E\frac{s}{r}}{1+\frac{1}{2}\left(\frac{\pi r}{n2l}\right)^2}\left\{\frac{1}{n^2\left[1+\left(\frac{n2l}{\pi r}\right)^2\right]^2}+\frac{n^2 s^2}{12r^2\left(1-\nu^2\right)}\left[1+\left(\frac{\pi r}{n2l}\right)^2\right]^2\right\}$$

(in cui consideriamo n=2… per esperienza!) introducendo i valori già indicati, e il modulo del titanio pari a 10500 Kg/mm$^2$, ricaviamo un valore

$$p_c = 280 bar$$

Correggiamo tale valore con un fattore $\frac{1}{1+0,5}=0,7$ per tener conto di una eccentricità dell'1% (vedi bibliografia) , confermando così i 200 bar richiesti.

Per completezza controlliamo anche il valore della sollecitazione in mezzeria :

$$\sigma = -\left(1-\frac{\nu}{2}\right)\frac{pr}{s} = -\frac{0,84\cdot 2\cdot 28}{0,8} = -60 kg/mm^2$$

Questi valori concordano con quanto ricavato nelle prove da noi eseguite: i galleggianti pressurizzati a 70 bar, collassano ad oltre 270 bar, come previsto.

Verifichiamo ora il comportamento alla temperatura di 380°C.

Il modulo elastico scende da 10500 a 8400 Kg/cm$^2$.

Poiché gli altri parametri restano costanti la pressione critica diminuisce in proporzione:

$$p_{ct} = 200\frac{8400}{10500} = 160 bar$$

Data la pressurizzazione a freddo e il tipo di miscela impiegata l’aumento della pressione interna è di circa 70 bar, sufficiente a compensare la riduzione pc - pct, pari a 200 - 160 = 40 bar.

Poiché il limite di snervamento si riduce circa il 35% del corrispondente a freddo (cioè molto più del modulo), verifichiamo anche questa circostanza; tenuto conto che la pressione interna a questa temperatura è 140 bar, per il funzionamento a 210 bar dobbiamo verificare la sollecitazione corrispondente a 70 bar:

$$\sigma = -\left(1-\frac{\nu}{2}\right)\frac{pr}{s} = -\frac{0{,}84\cdot 0{,}7\cdot 28}{0{,}8} = -20{,}5\,kg/mm^2$$

Anche questo valore è accettabile e in accordo con le prove.

Eseguendo lo stesso dimensionamento con acciaio inox avremmo ricavato uno spessore alquanto minore, cioè mm 0,6 invece di 0,8.

Ma ciò non servirebbe, per il semplice motivo che un galleggiante così fatto… non può galleggiare.

Infatti, detto m il numero di sezioni il peso P sarebbe:

$$P = mq\gamma + m\gamma 2\pi(2ls + h\delta) + 4\pi r^2 s\gamma + G$$

dove G è il peso del gruppo magnetico e della miscela di pressurizzazione, γ il peso specifico del materiale, e q il volume di apporto saldatura, (circa 300 mm$^3$ ogni tamburo).

La spinta di galleggiamento F è (tenendo conto della parte emersa):

$$F = \delta\left[\frac{2}{3}\pi r^3 + (2l+h)(m-2)\pi r^2\right]$$

dove δ è il peso specifico del liquido.

Poiché deve essere F = P, vediamo qual'è il valore di m necessario nei due casi (introducendo i valori, e passando a g e cm.):

Acciaio: $m(49{,}25\delta - 4{,}2\gamma) = 7{,}2\gamma + 52{,}5\delta + 85$

Titanio: $m(49{,}25\delta - 4{,}5\gamma) = 7{,}8\gamma + 52{,}5\delta + 85$

poiché è δ= 0,56 g/cm$^3$, nel caso dell'acciaio (γ= 8) il coefficiente di m è negativo e non c'è numero di tamburi che renda possibile il galleggiamento.

Per il titanio si ha invece :

$$m(27{,}6 - 20) = 35{,}7 + 29{,}4 + 85$$

da cui $m = 20$.
cioè il pezzo effettivamente costruito e impiegato.

Ultima notazione:
questo notevole concordare di calcoli e di effettivo comportamento è dovuto anche al tipo di costruzione, cioè sostanzialmente delle saldature che conferiscono al componente una rara omogeneità e rigidezza di struttura.

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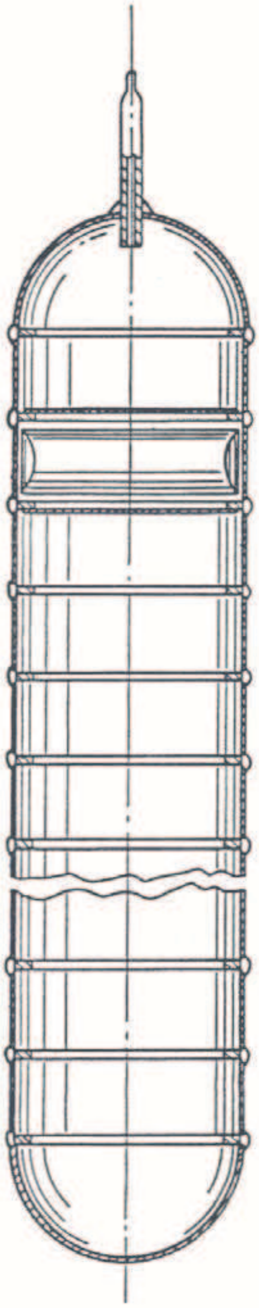

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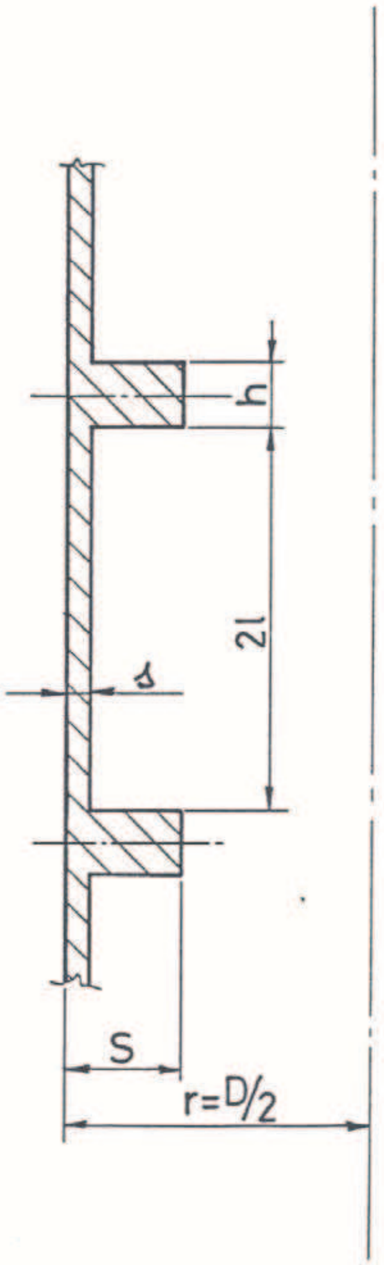

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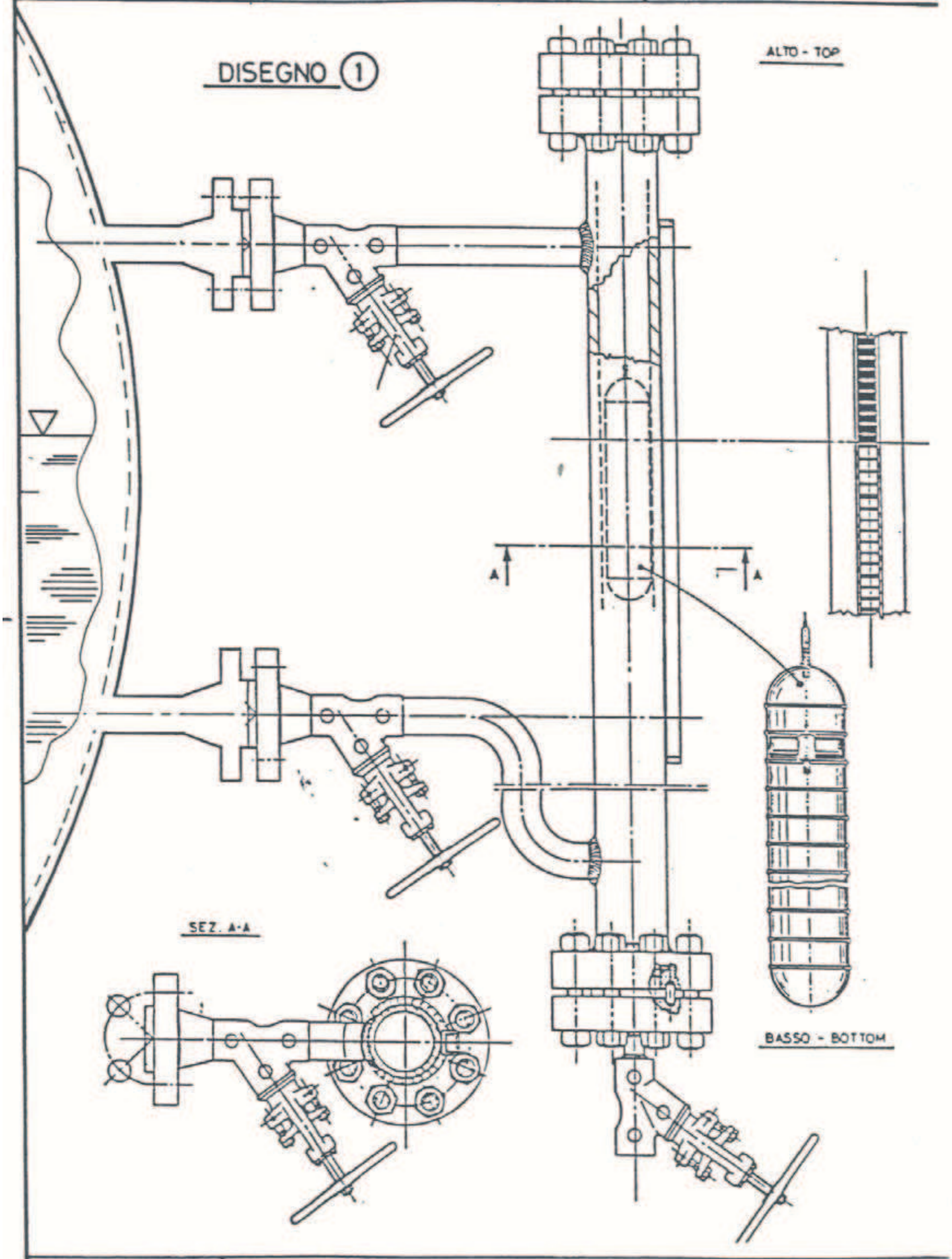

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| PREP. D. [illegible] Luigi | INDICATORI DI LIVELLO **BONT**®A<br>SENSORE MAGNETICO ADATTI PER<br>VAPORI D'ACQUA TIPO MAG-THR 210 | REV. No 0 |
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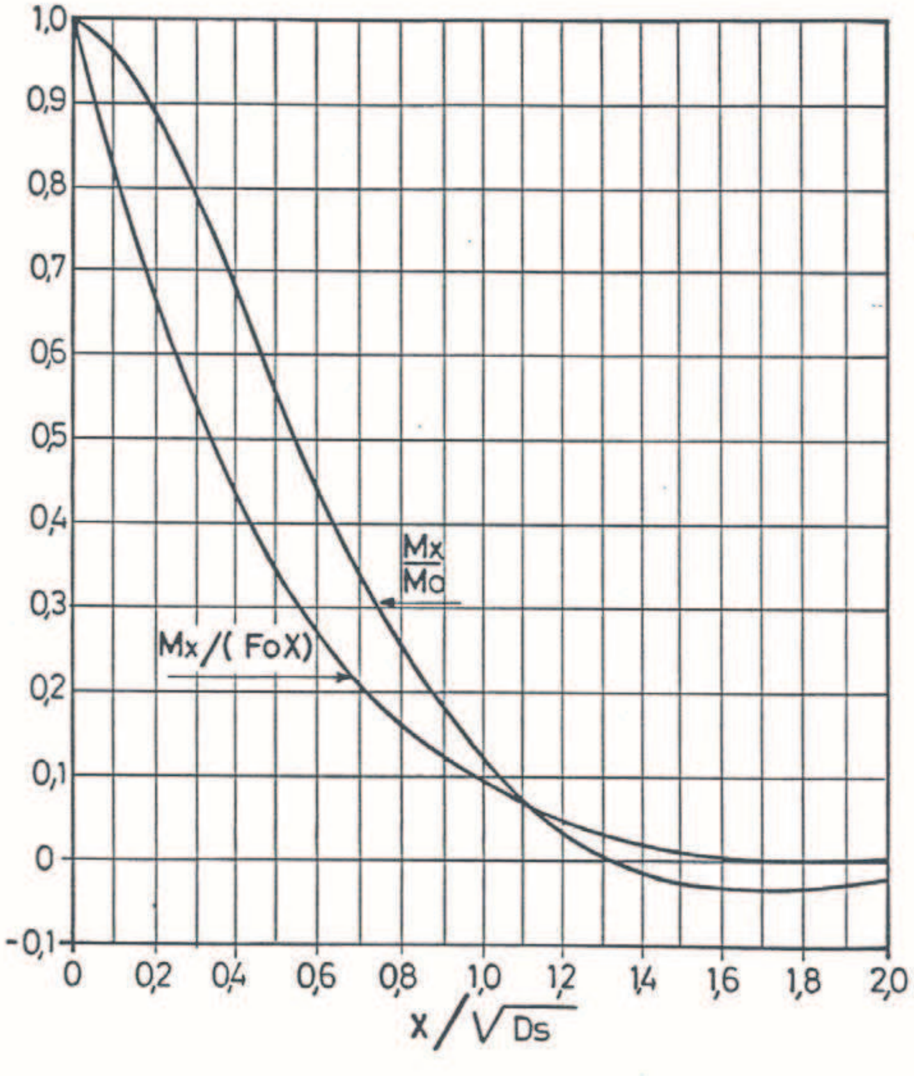
FIG.②

ANDAMENTO DEL MOMENTO FLETTENTE INDOTTO LUNGO LA DIREZIONE DELL'ASSE DEL CILINDRO PER EFFETTO DELL'IRRIGIDIMENTO SU UNA SEZIONE ( X= 0 )



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| APPR. | | PAG. 1 DI 1 |

# LA FORMATURA SUPERPLASTICA DELLE LEGHE DI TITANIO

L. CARRINO

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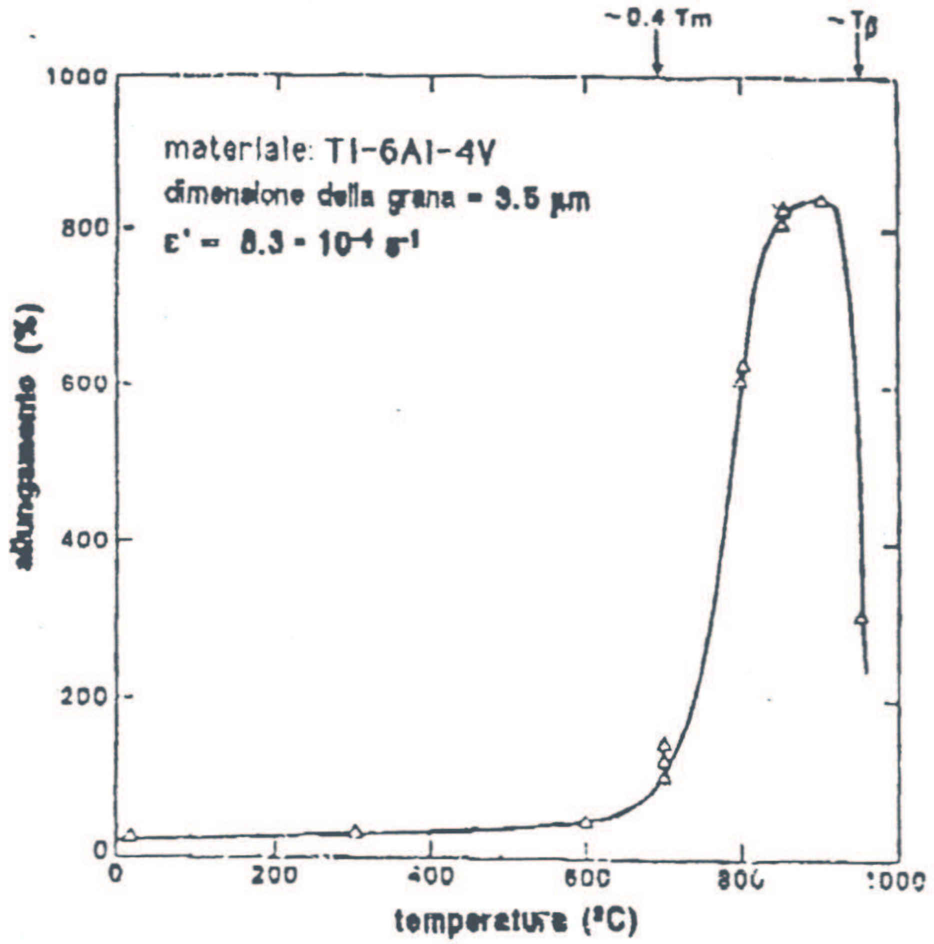
DI CASSINO

# SUPERPLASTICITA'

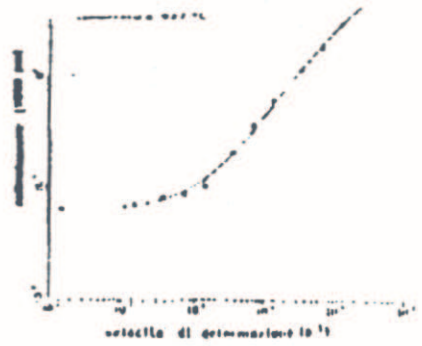
ECCEZIONALE DUTTILITA' ESIBITA DA CERTI MATERIALI ALLORQUANDO VENGONO DEFORMATI IN OPPORTUNE CONDIZIONI DI TEMPERATURA E VELOCITA' DI DEFORMAZIONE

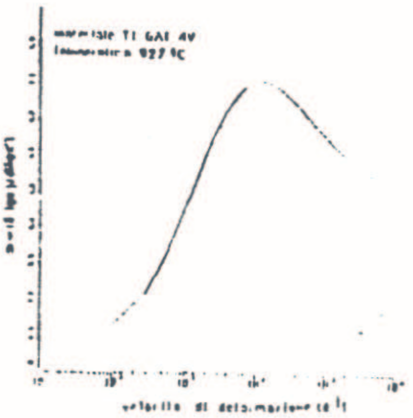
LA DUTTILITA' A TRAZIONE DEI METALLI SUPERPLASTICI E', TIPICAMENTE, COMPRESA FRA 200 E 1000%, MA, IN ALCUNI CASI, SONO STATI OTTENUTI ALLUNGAMENTI ANCHE DEL 5000%.

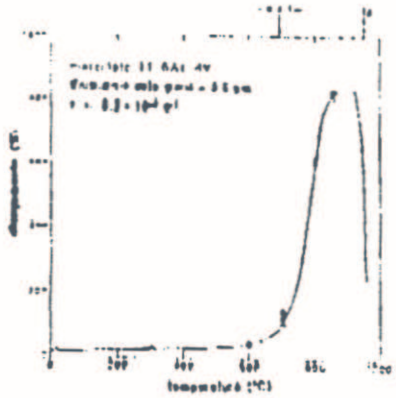
ALLUNGAMENTI DI QUESTO TIPO SONO DA UNO A DUE ORDINI DI GRANDEZZA SUPERIORI A QUELLI ORDINARIAMENTE OSSERVATI NEI MATERIALI METALLICI CONVENZIONALI E SONO MAGGIORMENTE CARATTERISTICI DEI MATERIALI PLASTICI.



L'ALLUNGAMENTO ASSUME I VALORI PIU' ELEVATI IN UN RISTRETTO CAMPO DI TEMPERATURE, AL DI FUORI DEL QUALE LA DUTTILITA' E' ALQUANTO MODESTA E ALL'INTERNO DEL CAMPO DI VALORI DEI MATERIALI METALLICI CONVENZIONALI.

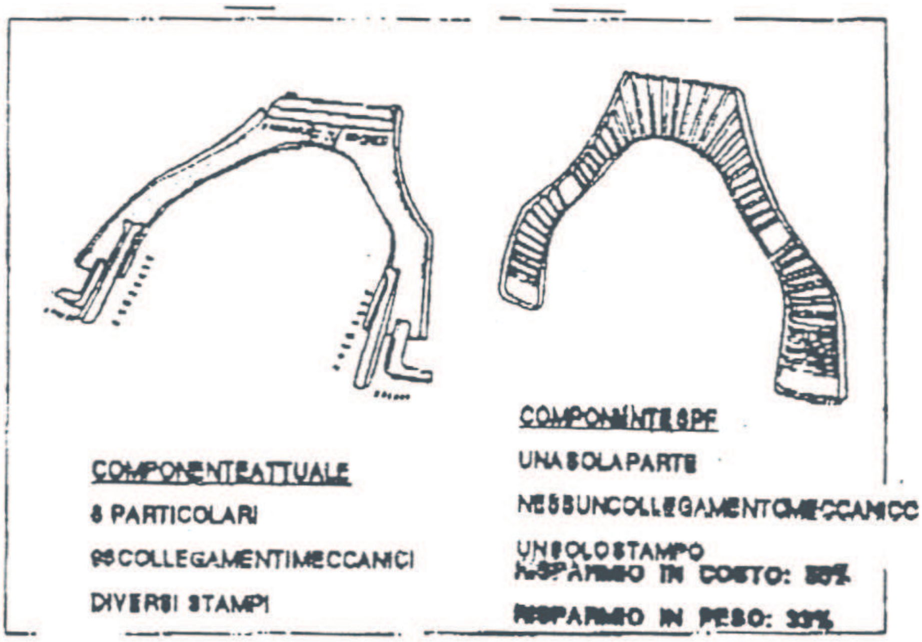






LE PRECEDENTI CARATTERISTICHE DELLE LEGHE METALLICHE SUPERPLASTICHE INDICANO ECCEZIONALI POTENZIALITA’ DI FORMATURA, MA METTONO ANCHE IN RISALTO LA NECESSITA’ DI UNO STRETTO CONTROLLO DEI PARAMETRI DI PROCESSO SE SI VOGLIONO SFRUTTARE TUTTE LE POSSIBILITA’ OFFERTE DA QUESTI STRAORDINARI MATERIALI.

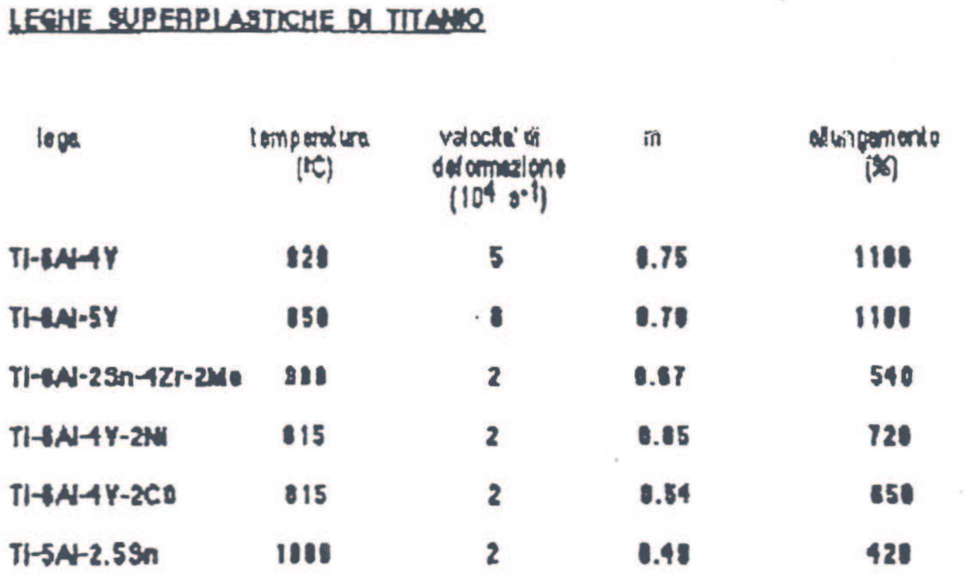
LA FORMATURA SUPERPLASTICA RICHIEDE CONTROLLI DI PROCESSO PIU’ RIGOROSI DEI CORRISPONDENTI PER I PROCESSI CONVENZIONALI E LA TECNOLOGIA E’ ALQUANTO PIU’ COMPLESSA, MA IN UN GRAN NUMERO DI APPLICAZIONI LA FORMATURA SUPERPLASTICA OFFRE CONSISTENTI VANTAGGI RISPETTO AD ALTRI METODI DI FABBRICAZIONE.



# LE LEGHE DI TITANIO PER LA FORMATURA SUPERPLASTICA

UNO DEI MAGGIORI OSTACOLI AD UN PIU’ ESTESO IMPIEGO DEI MATERIALI SUPERPLASTICI E’ LA RILUTTANZA DEI PROGETTISTI AD USARE MATERIALI DI CUI NON ESISTONO SPECIFICHE SUFFICIENTEMENTE CONSOLIDATE.

IL COMPORTAMENTO SUPERPLASTICO DELLE LEGHE DI TITANIO NON E’ COMPLETAMENTE NOTO, MA, FORTUNATAMENTE, QUESTE LEGHE SI DEFORMANO SUPERPLASTICAMENTE NELLA LORO COMPOSIZIONE ORDINARIA E COSI’ COME RESE DISPONIBILI DAI CICLI DI PRODUZIONE.



## LEGHE SUPERPLASTICHE DI TITANIO

| lega | temperatura (°C) | velocita' di deformazione ($10^{4}$ s$^{-1}$) | m | allungamento (%) |
|---|---|---|---|---|
| TI-6Al-4V | 920 | 5 | 0.75 | 1100 |
| TI-6Al-5V | 850 | 8 | 0.70 | 1100 |
| TI-6Al-2Sn-4Zr-2Mo | 900 | 2 | 0.67 | 540 |
| TI-6Al-4V-2Ni | 815 | 2 | 0.85 | 720 |
| TI-6Al-4V-2Co | 815 | 2 | 0.54 | 650 |
| TI-5Al-2.5Sn | 1000 | 2 | 0.48 | 420 |

Titolo:

# PROPRIETA' ANTIUSURA
# E APPLICAZIONI DEI RIVESTIMENTI PVD E CVD

AUTORE:

F. RABEZZANA - METEC, TORINO

## 1. INTRODUZIONE

Negli ultimi anni i processi di deposizione in fase vapore hanno avuto un notevole sviluppo per il rivestimento di una varietà di substrati diversi quali gli acciai legati, i carburi, le leghe di alluminio, le leghe di titanio, etc. con strati di carburi, nitruri, e altri composti refrattari.

La resistenza all'usura di questi substrati è stata incrementata notevolmente con l'utilizzo di questi rivestimenti sottili, sia per quanto riguarda l'usura abrasiva, adesiva e chimica sia per quanto riguarda i complessi meccanismi di usura presenti negli utensili da taglio. Ottimi risultati sono stati anche ottenuti nel campo della deformazione a freddo e su componenti meccanici critici dal punto di vista della resistenza all'usura.

In questo articolo vorremmo spiegare brevemente quali sono le principali caratteristiche dei processi di deposizione in fase vapore CVD e PVD e le loro principali applicazioni nel campo della resistenza all'usura.

## 2. CARATTERISTICHE DEI PROCESSI E DEGLI IMPIANTI CVD

Nei processi di “deposizione in fase vapore per via chimica” o CVD la deposizione dei film sottili avviene attraverso una reazione chimica, catalizzata dal substrato, che avviene in fase vapore in una regione molto vicina al substrato o sul substrato stesso.

Il materiale base viene riscaldato a una temperatura uguale alla temperatura di reazione dei gas presenti in modo da produrre la reazione di condensazione degli strati metallici o ceramici sul pezzo da ricoprire, e il riscaldamento viene eseguito con diversi metodi, normalmente a induzione o radiante. (In Fig. 1 è riportato uno schema di processo CVD).

Il deposito viene eseguito generalmente attraverso la riduzione di un alogenuro metallico che a contatto con la superficie del pezzo riscaldato forma progressivamente sulla superficie, per germinazione e accrescimento, dei composti metallici.

L’idrogeno è l’agente riduttore più comunemente usato. Il numero dei composti che si possono ottenere con il sistema CVD sono estremamente ampi, in Tab. 1 sono riportate le reazioni chimiche necessarie per l’ottenimento di alcuni dei più comuni di questi rivestimenti.

Questi composti hanno caratteristiche chimico-fisiche molto interessanti come un alto punto di fusione, un’elevata durezza, un basso coefficiente d’attrito, un’ottima stabilità chimica, caratteristiche che vengono sfruttate per risolvere problemi di usura, corrosione, resistenza alle alte temperature (vedi in Tab. 2 le caratteristiche di alcuni materiali usati nei processi CVD).

Numerosi Autori hanno dimostrato che la struttura e le proprietà dei rivestimenti sono anche strettamente legate ai parametri di processo, come la temperatura del substrato, la percentuale dei gas, e la pressione parziale dei gas di reazione.

Attualmente con le tecniche CVD si possono inoltre produrre rivestimenti multistrato combinando due o più materiali antiusura differenti (vedi in Fig. 2 una micrografia di un deposito multistrato TiC/TiN). Questa ultima innovazione prevede il ricoprimento dei particolari con strati successivi di differenti materiali antiusura in modo da contrastare nel migliore modo possibile tutti i tipi di usura presenti (adesiva, abrasiva e chimica) e nello stesso tempo garantire un'adesione elevata dei vari strati sul materiale base.

Le caratteristiche positive delle tecniche CVD sono soprattutto l'ottima aderenza del deposito dovuta anche a fenomeni di diffusione nel substrato; l'elevato potere penetrante con la possibilità di ricoprire pezzi con forme complesse, cavità e porosità; la facile variabilità della composizione dello strato di rivestimento e la formazione di strati ad elevata densità (bassa porosità); e infine l'estrema versatilità con la possibilità di rivestire contemporaneamente forme e geometrie differenti (vedi in Fig. 3 un esempio di carica di rivestimento CVD industriale).

I limiti maggiori di questa tecnica sono invece la bassa velocità di deposizione (2µm/h per il TiC e il TiN a 1000°C), sottoprodotti di reazione corrosivi (per es. HCl) e soprattutto le alte temperature di trattamento (850°-1100°C) e la conseguente necessità di ritrattare termicamente i particolari in acciaio rivestiti per riconferirgli le proprietà meccaniche originali con la conseguente deformazione (anche se minima) dei pezzi trattati.

Questa limitazione esclude per ora da questo tipo di rivestimento tutti i particolari in acciaio con tolleranze strette.

Un’ultima limitazione è il peggioramento (anche se lieve) della rugosità superficiale dei pezzi trattati, soprattutto nel caso di rugosità molto basse (superfici lappate). In questo caso occorre rilappare le superfici ricoperte dopo il processo CVD.

## 3. CARATTERISTICHE DEI PROCESSI E DEGLI IMPIANTI PVD

Nei processi di "deposizione in fase vapore per via fisica" o PVD la deposizione di film sottili antiusura avviene attraverso due fasi, la prima consiste nella evaporazione di metalli duri (per es. Ti) attraverso un processo di fusione sottovuoto o un bombardamento ionico del "target" o "bersaglio", la seconda consiste nella condensazione dei vapori sulla superficie del pezzo da rivestire.
Quando sono necessari dei rivestimenti di composti (carburi, nitruri, etc.) i vapori prodotti vengono fatti reagire con dei gas in modo da formare il composto desiderato.

Attualmente i processi PVD possono essere divisi in tre classi principali a seconda del metodo usato per vaporizzare il metallo e del tipo di percorso che segue il vapore prima di condensarsi sul substrato e precisamente: a) Evaporazione ad arco, b) Ion Plating con cannone, c) Sputtering (vedi in Fig. 4 lo schema dei vari processi). All'interno di queste tre classi principali esistono poi ancora delle differenziazioni dovute soprattutto alle differenti industrializzazioni di questi processi. In particolare, in base alle loro caratteristiche e alle realizzazioni attuali di impianti sono disponibili a livello industriale circa una decina di differenti impianti di rivestimento PVD (in Tab. 3 sono riportate le caratteristiche dei principali di questi impianti PVD).

Per spiegare in modo più approfondito le caratteristiche dei processi PVD consideriamo ora uno di questi processi e precisamente il sistema di “evaporazione ad arco” sviluppato in USA dalla Società “MULTI-ARC”.

Questa tecnologia è utilizzata di solito per rivestire dei substrati metallici anche se, utilizzando una polarizzazione del substrato a “radiofrequenza” o senza polarizzazione, è possibile rivestire materiali dielettrici, isolanti, ceramici.

La Fig. 5 mostra lo schema del processo mentre in Fig. 6 è riportato un tipo di impianto industriale derivato da questo processo.

L’esecuzione di un rivestimento di TiN con questo processo su un substrato ferro-so è ottenuto in 5 fasi successive.

La prima fase consiste nella preparazione delle superfici da rivestire che devono essere esenti da residui di oli, grassi, tracce di ossidazione, difetti di rettifica e qualsiasi altra contaminazione. Questa preparazione è eseguita attraverso metodi convenzionali quali una microsabbiatura e il successivo passaggio in una linea di sgrassaggio e pulitura attivata con ultrasuoni. Questa preparazione ha un'importanza fondamentale per assicurare una buona aderenza dei riporti sui substrati.

La seconda fase consiste nel posizionamento dei pezzi da rivestire negli appositi contenitori in modo che il plasma e i vapori metallici possano venire a contatto con tutte le superfici da rivestire, non esistono zone d'ombra, e sia assicurata così un'omogeneità nello spessore, nella struttura e nell'aderenza dei riporti.

Dopo il posizionamento dei pezzi viene eseguito un vuoto inferiore a $10^{-5}$ Torr all'interno della camera di rivestimento.

La terza fase consiste in un bombardamento ionico di ioni di Ti a forte energia per scaldare i pezzi e pulire le superfici al fine di aumentare l'aderenza dei successivi depositi. La tensione di polarizzazione applicata ai substrati in questa fase è dell'ordine di V = -1000 Volts e l'energia di impatto degli ioni di titanio è compresa fra 1 e 3 kev. In questo modo la superficie del substrato è perfettamente "decapata" per "polverizzazione", e degli ioni Ti ad alta energia possono localmente anche impiantarsi sulla superficie dei pezzi.

Gli ioni titanio che bombardano i substrati provocano il riscaldamento degli stessi per semplice trasferimento d'energia cinetica. I tempi di riscaldamento dipendono dalla massa dei pezzi, dalla pressione e dalla energia degli ioni. La temperatura di deposizione può essere compresa fra 175°C e 500°C in funzione dell'attitudine del substrato a sopportare tale temperatura (temperatura di fusione, temperatura di rinvenimento per gli acciai). Dei depositi perfettamente aderenti sono stati ottenuti con delle temperature di circa 200°C a causa della forte energia delle particelle incidenti (> 10ev) e del metodo di decapaggio ionico utilizzato.

La quarta fase consiste nella sintesi e nel rivestimento di nitruro di titanio.

L'elaborazione del deposito di TiN

si effettua in 3 tappe principali:

- l'emissione del vapore di Ti a partire dai catodi solidi
- il trasferimento sottovuoto dei vapori metallici
- la sintesi del composto stechiometrico TiN e la sua condensazione sul substrato.

Per quanto riguarda l'emissione del vapore in questo processo vengono creati degli archi elettrici sottovuoto sul catodo e il tipo di scarica utilizzata è caratterizzata per essere a bassa tensione ed elevata intensità di corrente. In questo modo l'emissione si effettua a partire da una zona molto localizzata e mobile denominata "spot catodico" dell'ordine di grandezza da 1 a 100µm di diametro sulla superficie del catodo. Successivamente gli "spot d'arco" si spostano in modo casuale su tutta la superficie del catodo ad una velocità superiore a 20-30 m/s.

Il movimento di questi spot può essere controllato utilizzando un campo magnetico.

La tensione utilizzata varia da 10 a 30 V (in Fig. 8 è riportata la scarica ad arco tra un catodo di titanio e un eccitatore).

Le principali particelle emesse attraverso una scarica ad arco sono degli elettroni del vapore metallico sotto forma di particelle neutre o di ioni e degli aggregati di atomi (data la natura molto esplosiva dell'arco). Le caratteristiche peculiari della scarica utilizzata nel processo PVD fanno si che una forte proporzione del vapore metallico prodotto sia ionizzato e che l'energia media degli ioni sia più elevata della tensione dell'arco.

Delle misure hanno mostrato che con questo processo più dell'80% del vapore emesso da un contatto di Ti è interamente ionizzato (vedi in Fig. 7 i tipi di scarica usati nei diversi processi PVD).

Dopo l'emissione avviene il trasferimento e l'accelerazione dei vapori metallici verso il substrato attraverso la tensione di polarizzazione (da 0 a -500 V). Le diverse collisioni tra le molecole gassose riducono l'energia media delle particelle e aumentano il tempo di trasferimento tra la sorgente ed il substrato, inoltre dei meccanismi di eccitazione, trasferimento d'elettroni, dissociazione e sintesi operano simultaneamente nella fase di creazione del "plasma".

L'ultima tappa di questa quarta fase

è la sintesi del TiN seguita dalla sua condensazione sul substrato. La condensazione delle particelle di Ti accompagnata dal fenomeno di assorbimento dell'azoto sul Ti avviene in vicinanza e sul substrato stesso. Contemporaneamente avviene un bombardamento di ioni di $Ti^+$ che attiva le reazioni di superficie, aumenta l'aderenza dello strato e aumenta anche la densità della struttura dello strato stesso.
La quinta e ultima fase del processo di rivestimento consiste nel raffreddamento e nell'uscita dei pezzi rivestiti dall'impianto.

Le caratteristiche positive della tecnica di rivestimento PVD sono soprattutto la estrema variabilità nella composizione dei riporti, la possibilità di variazione nella temperatura di riscaldamento del substrato, la velocità di rivestimento molto elevata con depositi ad elevata purezza, il controllo della microstruttura del rivestimento ed infine la eccellente finitura superficiale (praticamente uguale a quella del substrato).

## 4. CAMPI DI APPLICAZIONE DELLE TECNOLOGIE CVD E PVD NEL SETTORE DELLA RESISTENZA ALLA USURA

L’applicazione dei processi CVD è concentrata ancora notevolmente nel rivestimento degli inserti per asportazione di truciolo in carburo. In questo campo i rivestimenti multistrato hanno avuto molto successo e sono stati sperimentati ricoprimenti multipli con 7 - 10 strati successivi di materiali antiusura differenti. Come esempio possiamo citare il rivestimento con strati di A1203 su films di TiC e TiN nel caso di inserti utilizzati ad elevate condizioni di taglio. L’A1203 ha una elevata resistenza all’usura meccanica e una stabilità chimica alle alte temperature anche elevata, molto utile alle alte velocità di taglio dove è maggiore il rischio di ossidazione e diffusione tra il materiale da lavorare e il tagliente dell’utensile.

Oltre a questo settore i campi di applicazione dei rivestimenti CVD ad alta temperatura sono soprattutto il settore della deformazione plastica a freddo (estrusione, tranciatura, etc.) e il settore dell’utensileria da taglio laddove non ci sono tolleranze dimensionali molto strette con il vantaggio di abbassare il coefficiente d’attrito, ridurre l’usura, aumentare la vita e la produttività degli utensili; la formazione di strati ad elevata durezza per ridurre l’usura di componenti meccanici; la produzione di strati protettivi contro la corrosione o l’ossidazione ad alte temperature; barriere di diffusione e barriere termiche.

L’applicazione dei processi PVD è estesa ormai a quasi tutti gli utensili in acciaio rapido e in particolare i maggiori successi sono stati ottenuti con gli utensili aventi una geometria complessa e un costo elevato (creatori, brocce, etc.). Ottimi risultati sono stati ottenuti anche nel campo della deformazione plastica a freddo con il rivestimento di punzoni e matrici aventi tolleranze dimensionali strette o con requisiti di rugosità superficiali molto elevati (lappatura).

In Fig. 9 è riportato l’incremento medio di durata utile (in %) ottenuto su differenti categorie di utensili, mentre in Fig. 10 sono riportati alcuni risultati industriali di applicazioni su particolari tipi di utensileria.

Oltre a questi campi di applicazione l’utilizzo dei rivestimenti PVD si sta estendendo in campi molto diversificati fra loro per migliorare le caratteristiche antiusura dei componenti in acciaio o in carburo. Come esempi possiamo citare le applicazioni nella industria tessile (camme, guida fili), nella industria della carta (lame o cilindri da taglio), nell’industria alimentare (viti di alimentazione), nell’industria biomedica (protesi, utensili chirurgici), nell’industria aeronautica e spaziale (cuscinetti), nell’oreficeria e coltelleria (vedi alcuni esempi in Figura 11).

Per quanto riguarda le applicazioni nell’industria biomedica, il rivestimento di protesi con strati di TiN riduce notevolmente il coefficiente d'attrito, aumenta la durezza superficiale e riduce l’interazione dei liquidi biologici con metalli, diminuendo il rischio di rigetto. Nel caso invece dell’oreficeria e coltelleria il rivestimento di TiN aumenta la resistenza all’usura (rigature), alla nebbia salina e all’aggressione del sudore.

$$2AlCl_3 + 3CO_2 + 3H_2 \longrightarrow Al_2O_3 + 3CO + 6HCl$$

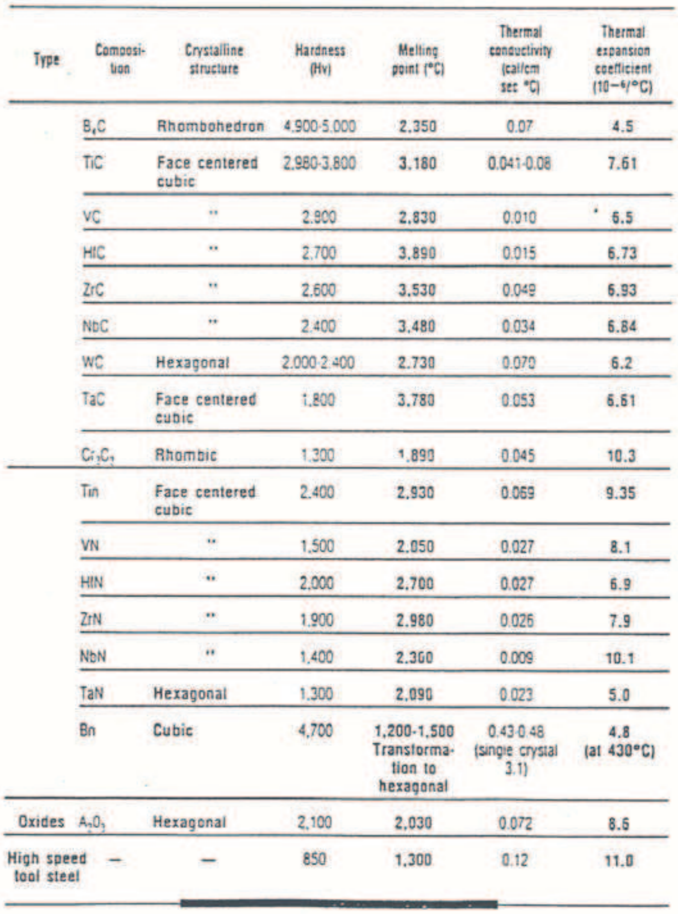
$$TiCl_4 + 2H_2 + \frac{1}{2} N_2 \longrightarrow TiN + 4HCl$$

$$TiCl_4 + CH_4 \longrightarrow TiC + 4HCl$$

$$TiCl_4 + 2H_2 + 2CO_2 \longrightarrow TiO_2 + 2CO + 4HCl$$

$$ZrCl_4 + 2CO_2 + 2H_2 \longrightarrow ZrO_2 + 4HCl + 2CO$$

Tab.I Alcuni rivestimenti prodotti con la tecnica CVD e relative reazioni chimiche.



| Type | Composition | Crystalline structure | Hardness (Hv) | Melting point (°C) | Thermal conductivity (cal/cm sec °C) | Thermal expansion coefficient (10−⁶/°C) |
|---|---|---|---|---|---|---|
| | $B_4C$ | Rhombohedron | 4.900-5.000 | 2.350 | 0.07 | 4.5 |
| | TiC | Face centered cubic | 2.980-3.800 | 3.180 | 0.041-0.08 | 7.61 |
| | VC | " | 2.900 | 2.830 | 0.010 | 6.5 |
| | HIC | " | 2.700 | 3.890 | 0.015 | 6.73 |
| | ZrC | " | 2.600 | 3.530 | 0.049 | 6.93 |
| | NbC | " | 2.400 | 3.480 | 0.034 | 6.84 |
| | WC | Hexagonal | 2.000-2.400 | 2.730 | 0.070 | 6.2 |
| | TaC | Face centered cubic | 1.800 | 3.780 | 0.053 | 6.61 |
| | $Cr_3C_2$ | Rhombic | 1.300 | 1.890 | 0.045 | 10.3 |
| | Tin | Face centered cubic | 2.400 | 2.930 | 0.069 | 9.35 |
| | VN | " | 1.500 | 2.050 | 0.027 | 8.1 |
| | HIN | " | 2.000 | 2.700 | 0.027 | 6.9 |
| | ZrN | " | 1.900 | 2.980 | 0.026 | 7.9 |
| | NbN | " | 1.400 | 2.360 | 0.009 | 10.1 |
| | TaN | Hexagonal | 1.300 | 2.090 | 0.023 | 5.0 |
| | Bn | Cubic | 4,700 | 1,200-1,500 Transformation to hexagonal | 0.43-0.48 (single crystal 3.1) | 4.8 (at 430°C) |
| Oxides | $A_2O_3$ | Hexagonal | 2,100 | 2,030 | 0.072 | 8.6 |
| High speed tool steel | — | — | 850 | 1,300 | 0.12 | 11.0 |

Tab.II Caratteristiche di alcuni materiali usati nei processi CVD

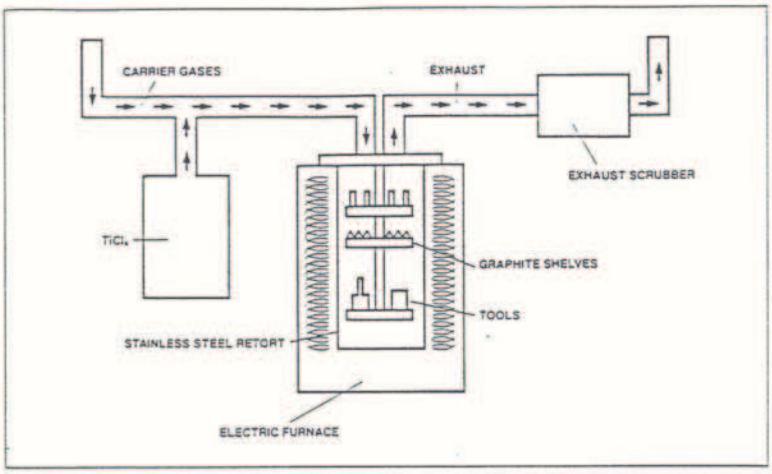


Fig.1 Schema di un processo CVD (proc.Scientific Coatings)

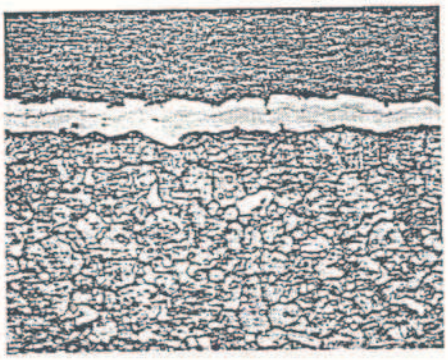


Fig.2 Micrografia (500x)di un deposito TiC/TiN su un substratoin M2

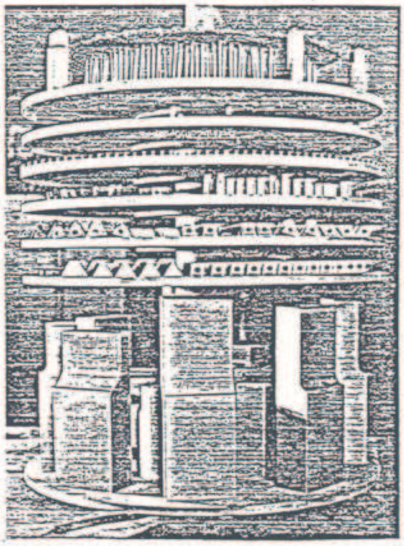


Fig.3 Esempio di carica industriale CVD

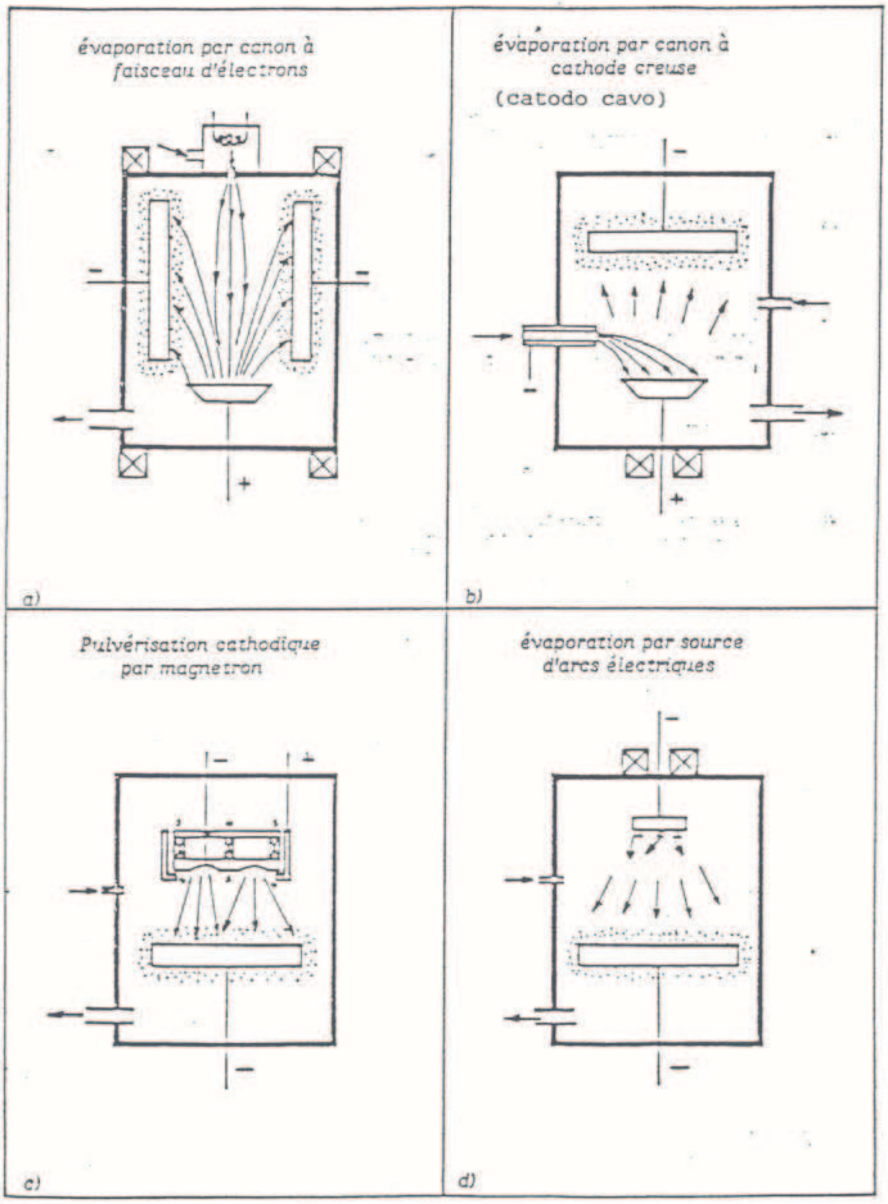
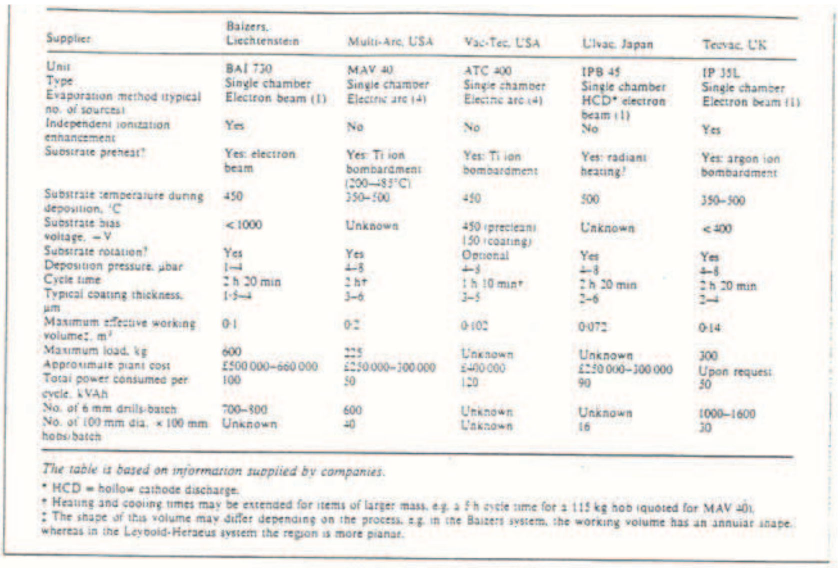


Fig.4 Schema dei differenti processi PVD (a e b =Ion Plating , c = Sputtering,d = evaporazione ad arco)



| Supplier | Balzers, Liechtenstein | Multi-Arc, USA | Vac-Tec, USA | Ulvac, Japan | Tecvac, UK |
|---|---|---|---|---|---|
| Unit | BAI 730 | MAV 40 | ATC 400 | IPB 45 | IP 35L |
| Type | Single chamber | Single chamber | Single chamber | Single chamber | Single chamber |
| Evaporation method (typical no. of sources) | Electron beam (1) | Electric arc (4) | Electric arc (4) | HCD* electron beam (1) | Electron beam (1) |
| Independent ionization enhancement | Yes | No | No | No | Yes |
| Substrate preheat? | Yes: electron beam | Yes: Ti ion bombardment (200–485°C) | Yes: Ti ion bombardment | Yes: radiant heating† | Yes: argon ion bombardment |
| Substrate temperature during deposition, °C | 450 | 350–500 | 450 | 500 | 350–500 |
| Substrate bias voltage, −V | < 1000 | Unknown | 450 (preclean)<br>150 (coating) | Unknown | < 400 |
| Substrate rotation? | Yes | Yes | Optional | Yes | Yes |
| Deposition pressure, µbar | 1–4 | 4–8 | 4–8 | 4–8 | 4–8 |
| Cycle time | 2 h 20 min | 2 h† | 1 h 10 min† | 2 h 20 min | 2 h 20 min |
| Typical coating thickness, µm | 1·5–4 | 3–6 | 3–5 | 2–6 | 2–4 |
| Maximum effective working volume‡, m³ | 0·1 | 0·2 | 0·102 | 0·072 | 0·14 |
| Maximum load, kg | 600 | 225 | Unknown | Unknown | 300 |
| Approximate plant cost | £500 000–660 000 | £250 000–300 000 | £400 000 | £250 000–300 000 | Upon request |
| Total power consumed per cycle, kVAh | 100 | 50 | 120 | 90 | 50 |
| No. of 6 mm drills/batch | 700–800 | 600 | Unknown | Unknown | 1000–1600 |
| No. of 100 mm dia. × 100 mm hobs/batch | Unknown | 40 | Unknown | 16 | 30 |

*The table is based on information supplied by companies.*

* HCD = hollow cathode discharge.

† Heating and cooling times may be extended for items of larger mass, e.g. a 5 h cycle time for a 115 kg hob (quoted for MAV 40).

‡ The shape of this volume may differ depending on the process, e.g. in the Balzers system, the working volume has an annular shape, whereas in the Leybold-Heraeus system the region is more planar.

Tab.III Caratteristiche dei principali impianti PVD(Fon.A.Matthews)

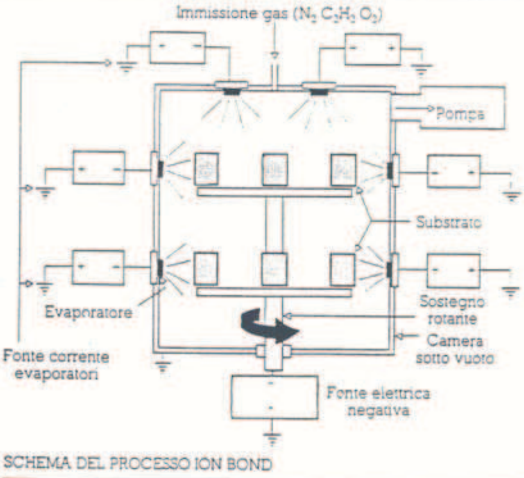


Fig.5 Schema del processo PVD di evaporazione ad arco MULTI-ARC

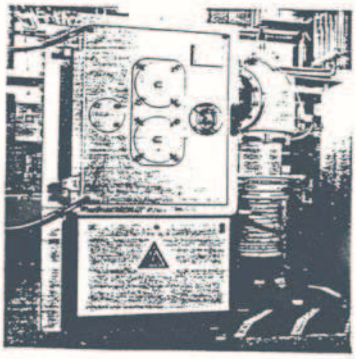


Fig.6 Impianto industr. PVD MULTI-ARC

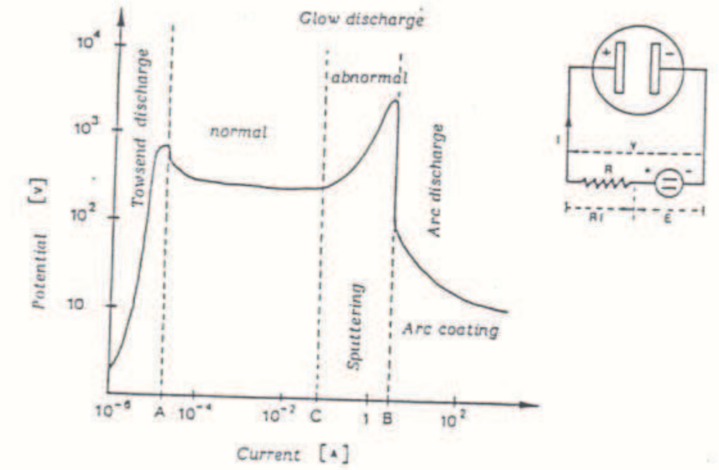


Fig.7 Tipi da scarica utilizzati nei differenti processi PVD

Fig.8 Scarica ad arco
tra un catodo in Ti
e un eccitatore

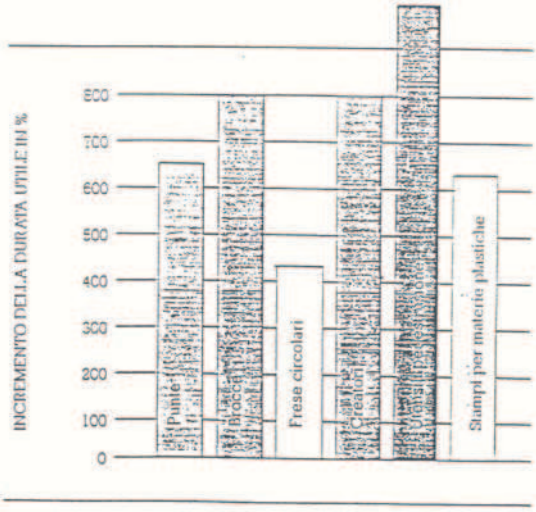


Fig.9 Incremento medio di durata utile (in %)
su differenti categorie di utensili con
rivestimenti PVD-TiN MULTI-ARC

| **PUNTA**<br>Ø 8 x 117 mm | **BROCCIA**<br>300 mm | **FRESE CIRCOLARI**<br>Ø 150 x 26 mm | **CREATORI**<br>Ø 60 x 110 mm | **PUNZONI**<br>86 x 85 mm | **MATRICI E STAMPI PER MATERIE PLASTICHE** |
|---|---|---|---|---|---|
| MATERIALE<br>HSS | MATERIALE<br>ASP | MATERIALE<br>HSS | MATERIALE<br>DMo5 | MATERIALE<br>.2343 | MATERIALE<br>RAB 1 |
| MATERIALE LAVORATO<br>42 Cr Mo 4<br>Resistenza 1000 N/mm 2 | MATERIALE LAVORATO<br>Acciaio al Cromo | MATERIALE LAVORATO<br>BZ 90 | MATERIALE LAVORATO<br>C45 ÷ C50 | MATERIALE LAVORATO<br>19 Mn 4 | MATERIALE LAVORATO<br>Bachelite |
| Rendimento non Ricoperto<br>34 Fori passanti<br>Piastre 30 mm V = 25 m/min<br>S = 0.09 mm | Rendimento non Ricoperto<br>2000 pezzi per affilatura | Rendimento non Ricoperto<br>214 pezzi per affilatura | Rendimento non Ricoperto<br>V = 90 m/min | Rendimento non Ricoperto<br>0 pezzi | Rendimento non Ricoperto<br>48.000 colpi inizio usura<br>dopo 150.000 colpi non più utilizzabile |
| Rendimento Ricoperto<br>219 Fori passanti<br>Piastra 30 mm.<br>V = 25 m/min S = 0.09 mm | Rendimento Ricoperto<br>ca. 16.000 pezzi<br>per riaffilatura | Rendimento Ricoperto<br>918 pezzi<br>per riaffilatura | Rendimento Ricoperto<br>durata 8 volte superiore dopo<br>la 1ª riaffilatura<br>durata 3-4 volte superiore | Rendimento Ricoperto<br>10.000 ÷ 15.000 pezzi | Rendimento Ricoperto<br>300.000 colpi senza<br>usura manifesta |

Fig.10 Risultati industriali di applicazioni dei rivestimenti PVD-TiN MULTI-ARC su alcuni tipi di utensileria

Fig.11 Alcuni campi di applicazione dei rivestimenti PVD

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# ELECTROCHEMISTRY OF TITANIUM IN MOLTEN SALTS

The Institute of Electrochemistry of the Ural Department of the USSR Academy of Science, which I am representing here, is the leading academic institution in the Soviet Union in the sphere of fundamental investigations of high temperature electrochemical processes both in molten and solid electrolytes.

Considerable investigations in the sphere of electrochemistry of titanium have been made byour scientists, namely, metal titanium have been investigated and in the dependence of valency of titanium ions, as an essential potential determining ion in the melt, on the cations composition of salt-solvent has been obtained.

The electrode-equilibrium potentials of titanium have been determined and the dependence of their magnitude on a cation-radius of salt-solvent of electrolyte has been investigated.

The investigations on thermodynamics and kinetics of electrode processes under the anodic dissolution and the cathodic deposition of titanium have been made and the electrochemical behaviour of nitrides, carbides, oxide-carbonaceous compositions of titanium has been studied.

A magnitude of vapour pressure of titanium tetrachloride in the equilibrium state with molten halogenides of alkali metals has been measured and the dependence of the titanium content in the melt for the given composition of the molten salts and the temperature on the vapour pressure of titanium tetrachloride above the melt has been determined.

A structure of cathodic deposition of titanium and the influence (i.e. size, grain forms, purity) of the electrolyte composition and electrolysis regimes has been studied. The compact titanium production, as layers of considerable thickness, which can be employed as well as coatings.

Thus, to obtain a process of titanium deposition on the cathode, it is necessary to reduce a four valent ion of titanium to lower valent forms. In fluorine and fluoride chloridric melts a high concentration of tetrachloride of titanium may be done, but one can see from high complex forming properties of these melts the difficult forming low components of titanium are formed and, consequently, this fact produces difficulties in electrode processes.

We have works based on these fundamental investigations. This fact permits to obtain titanium coatings, i.e. to deposit films on titanium and these films protect from corrosion and to obtain powders of alloys on the basis of titanium.

We suppose that this complex with the results on physico-chemistry and electrochemistry of titanium in melts can be used for the development of technologies to obtain titanium from its halogenides and, possibly, also oxides by electrochemical way bypassing the process of metallothermie.

Thus, the works made by G.T.T. firm on titanium are interesting for USSR and we think that our cooperation will be useful in this domain.

Thank you for your attention.

Gianmichele Orsello
Ginatta Torino Titanium

# AVANZAMENTO DELLE ATTIVITA' DELLA GTT NELL'INDUSTRIA DEL TITANIO

Gentili Signore e Signori,

La giornata volge al termine, abbiamo ascoltato molte interessanti relazioni sulla produzione, lavorazione, applicazioni, caratteristiche del titanio e delle sue leghe. Io vorrei parlarVi pochi minuti della nostra azienda, la GTT che, come sapete, fa parte del gruppo Ginatta, in particolare di che cosa facciamo per la produzione e promozione del titanio.

La Ginatta da molti anni opera nello sviluppo delle tecnologie metallurgiche ed energetiche che si fondano sulla elettrochimica: in particolare le batterie tradizionali, le batterie innovative al sodio-zolfo, le pile combustibili, i generatori radicalmente innovativi a sali fusi, la produzione di piombo elettrolitico e, naturalmente, la produzione e lo sviluppo del titanio.

Prima di parlare di titanio vorrei cogliere l’occasione per segnalare che fra due settimane vi sarà un nuovo convegno qui a Torino, organizzato dalla Ginatta per promuovere e informare il mondo dell’industria sui processi e impianti della Ginatta relativi al piombo e alle batterie e sui nuovi usi del piombo.

Titanio. Avete ascoltato stamane una relazione di funzionari della Titania, la società del gruppo ILVA che ha acquistato la nostra tecnologia per la produzione di titanio elettrolitico. L’Italimpianti, quale General Contractor, sta realizzando per la Titania l’impianto produttivo. La GTT è responsabile della fornitura dell’impianto di elettrolisi, ossia delle celle elettrolitiche che, alimentate con tetracloruro di titanio, producono il titanio grezzo: i cristalli di titanio.

Oggi avete sentito parlare più volte della spugna di titanio: i cristalli di titanio, come la spugna di titanio, sono il titanio grezzo, ma abbiamo preferito chiamarli con un nome diverso perché le caratteristiche morfologiche e chimiche sono diverse. Come avete sentito stamane da Mr. Callaghan della RMI, i cristalli di titanio hanno contenuti di volatili pari al 50% delle migliori spugne tradizionali, basso contenuto di ossigeno e azoto, basse impurezze metalliche. Nella figura 1 vediamo la spugna come esce dagli impianti tradizionali, mentre nella figura 2 vediamo i cristalli di titanio.

H0 parlato di celle e di elettrolisi: in figura (3) vedete il ciclo di produzione dal minerale al lingotto. La cella elettrolitica (Fig. 4) illustrata è il Modex III, l’impianto di Santena. Questo impianto è stato realizzato nell’86 ed è servito per mettere a punto la tecnologia (Fig. 5) e a fare campagne di produzione pilota per noi o per i nostri clienti.

La sala di controllo (Fig. 6) e il manipolatore per il movimento degli elettrodi (Fig. 7) sono parti importanti dell’impianto.

Abbiamo raggiunto la dimensione e la produzione industriale della cella di elettrolisi con l’impianto Modex IV. Le immagini che seguono sono fotografie del Modex IV che abbiamo installato presso lo stabilimento della RMI ad Ashtabula in Ohio.

La dimensione della cella industriale è apprezzabile in queste immagini, i vari piani di lavoro (Fig. 8), la cabina di controllo, osservate il piano operativo dove l’operatore controlla l’avvicendarsi dei catodi sui quali si produce titanio e che vengono scortecciati, ossia privati del loro prodotto in un’apposita macchina situata all’interno della stessa cella elettrolitica. Vedete il bocchello dalla quale viene estratto il titanio dalla cella, osservate l’alimentazione elettrica alla cella con corrente di alta intensità (100.000 A) a bassa tensione.
La parte superiore della cella, le pompe e i quadri elettrici del Motor Control Centre completano l’impianto.
Osserviamo all’interno i catodi e gli anodi posizionati in cella durante la produzione. Ancora uno sguardo esterno e al laboratorio fuori linea dove un tecnico effettua le analisi necessarie al controllo del processo.

Avete notato qui all’ingresso, il modello di due moduli industriali da quattro celle, che costituiscono le unità produttive dell’impianto che stiamo realizzando per la società Titania, come avete sentito stamane nella relazione del Rag. Timpani e dell’Ing. Proface della Italimpianti. In Fig. 9 vediamo i due moduli nell’insieme, uniti dalla dry box; in Fig. 10 osserviamo il dettaglio di precamera, parte della precamera, stripper e scarico del titanio prodotto.

Il titanio estratto dalla cella viene lavato del contenuto di sale ed essiccato; a questo punto è pronto per essere rifuso in lingotti con o senza aggiunte di particolari metalli di lega.

Sono evidenti il notevole impegno dei collaboratori della Ginatta e gli ingenti investimenti che sono stati effettuati per lo sviluppo di questa tecnologia completamente innovativa a partire dalle prime prove di laboratorio degli anni ‘70, fino allo sviluppo impiantistico prototipale e pilota dell’inizio degli anni ‘80 fino ad oggi.

Questo è il flusso di materiale e operazioni necessarie per trasformare il lingotto nel semilavorato in titanio o leghe che il progettista potrà utilizzare (Fig. 11).

La rifusione del titanio in lingotti (Fig. 12) in forni “VAR” è una tecnologia oggi consolidata in vari paesi europei, negli Stati Uniti e in Giappone. In Italia è stato necessario affrontare anche da parte nostra questo tema, per essere nelle condizioni di contribuire all’avviamento dei grandi forni che completeranno l'impianto di Terni.

Ezio Debernardi ha già parlato del forno che noi utilizziamo per poter fornire piccoli quantitativi di titanio o leghe ai clienti (Fig. 13 e 14). Nella cabina di controllo (Fig. 15) computer e plc guidano la fusione.

Abbiamo così illustrato le attività dei settori della GTT per l’ingegneria elettrochimica, lo sviluppo di processo e di impianto e la fusione e lavorazione del titanio.
Il controllo di qualità (Fig. 16) nei nostri laboratori è accurato, e reso più semplice dal controllo computerizzato degli impianti.

Non vi sarà sfuggito certamente il fatto che il tetracloruro di titanio è un sale, che viene prodotto a partire dal rutilo, il biossido minerale di titanio. Questa produzione viene effettuata nell’impianto chimico di carboclorurazione. Avete ascoltato da Mr. Wilde della società Minproc le caratteristiche della estrazione mineraria del rutilo in Australia, alcune notizie circa l’impianto di carboclorurazione del minerale e gli usi del tetracloruro di titanio.

Anche questa tecnologia è stata da noi studiata per fornire un contributo di sviluppo ingegneristico e impiantistico per l’impianto Italiano e per altri impianti allo studio in vari paesi del mondo.
Una parte del nostro gruppo di ingegneria è dedicato a tale attività.

Per quanto riguarda le forniture di titanio sul mercato in questi anni abbiamo contribuito con una quota piccola, ma noi riteniamo significativa, all’uso del titanio e allo sviluppo di certe applicazioni (Fig. 17), vendendo da magazzino. In questi mesi siamo impegnati, in collaborazione con la Titania, a sviluppare un’organizzazione di vendita di semilavorati sia da magazzino sia su commessa in titanio e nelle principali leghe di titanio.

Abbiamo contribuito in questi anni, come è stato detto dall'Ing. D'Angelo del Centro Sviluppo Materiali, alla realizzazione di vari programmi di sviluppo delle lavorazioni del titanio in collaborazione anche con altri Enti come l'Enea, Università e Centri di Ricerca Italiani.

Il nostro gruppo è a disposizione di chiunque per fornire materiale, informazioni, suggerire lavorazioni, realizzare in proprio con la Vostra collaborazione prototipi.

Per il prossimo anno ci siamo dati, insieme alla società Titania, l'obiettivo di incrementare le vendite di semilavorati di titanio. Nel 1991 entreranno in funzione i primi due moduli dell'impianto Titania con la produzione di 1400 t di titanio. Nel 1992 entreranno in funzione gli altri moduli per oltre 2800 t di titanio.

Per chi è abituato all'acciaio queste cifre appaiono piccole. Per chi conosce il titanio invece queste cifre sono importanti. In realtà il mercato industriale non aerospaziale dei consumi di titanio è cresciuto costantemente dell'8-9% all'anno in Europa e negli U.S.A. I prezzi sono aumentati in questi ultimi mesi a causa dell'aumentare delle richieste del mercato e dell'incapacità degli attuali produttori e commercianti di soddisfare tutte le richieste. Nel 2000, con una crescita di questo tenore, che è stata ormai confermata, si utilizzeranno oltre 200.000 t di semilavorati di titanio in tutto il mondo, contro le 60-70.000 dell'88.

Gli impianti di produzione realizzati con la nostra tecnologia in Italia, in America e in altre parti del mondo daranno quindi un contributo che noi ci auguriamo significativo alla diffusione delle applicazioni del titanio in tutto il mondo.

Grazie per l'attenzione

GOINT89-PC14

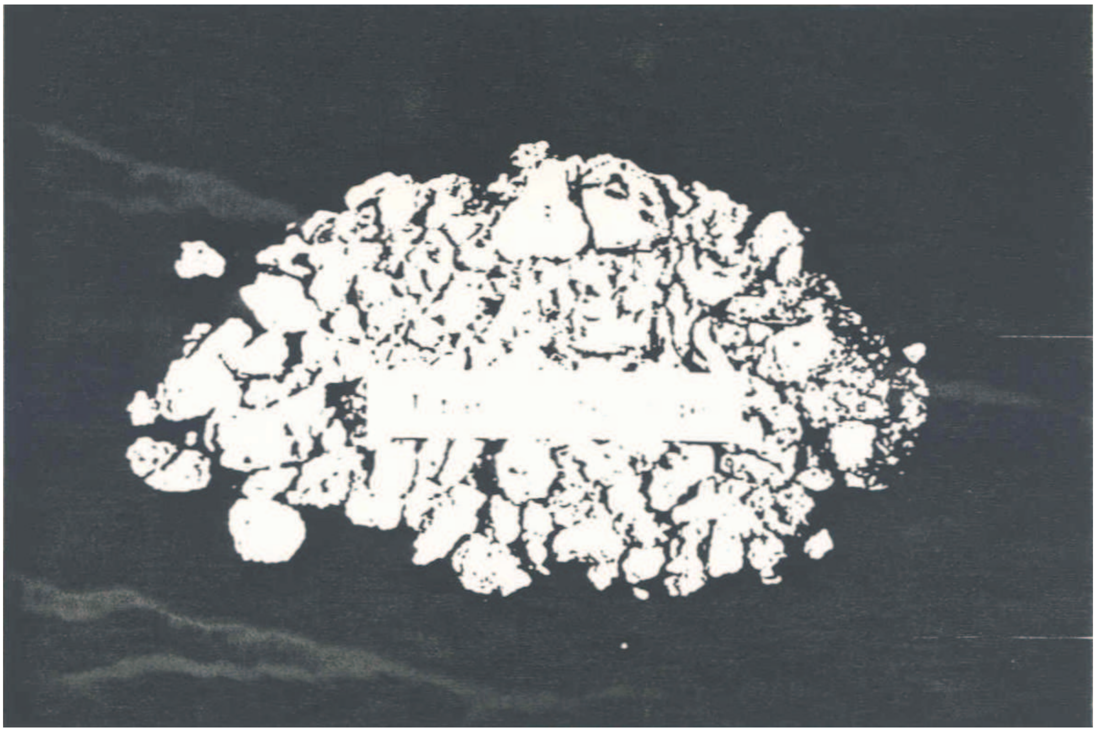

Fig. 1 - Spugna di titanio prodotta da impianti tradizionali

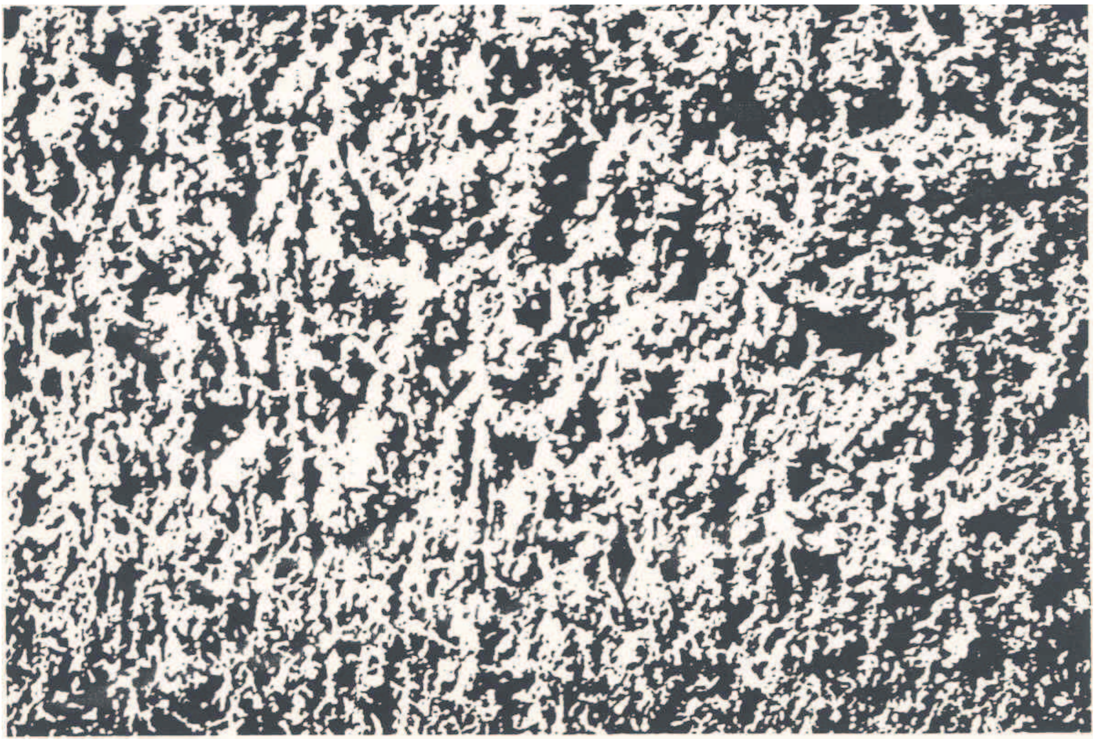

Fig. 2 – Cristalli di titanio prodotti con processo Ginatta

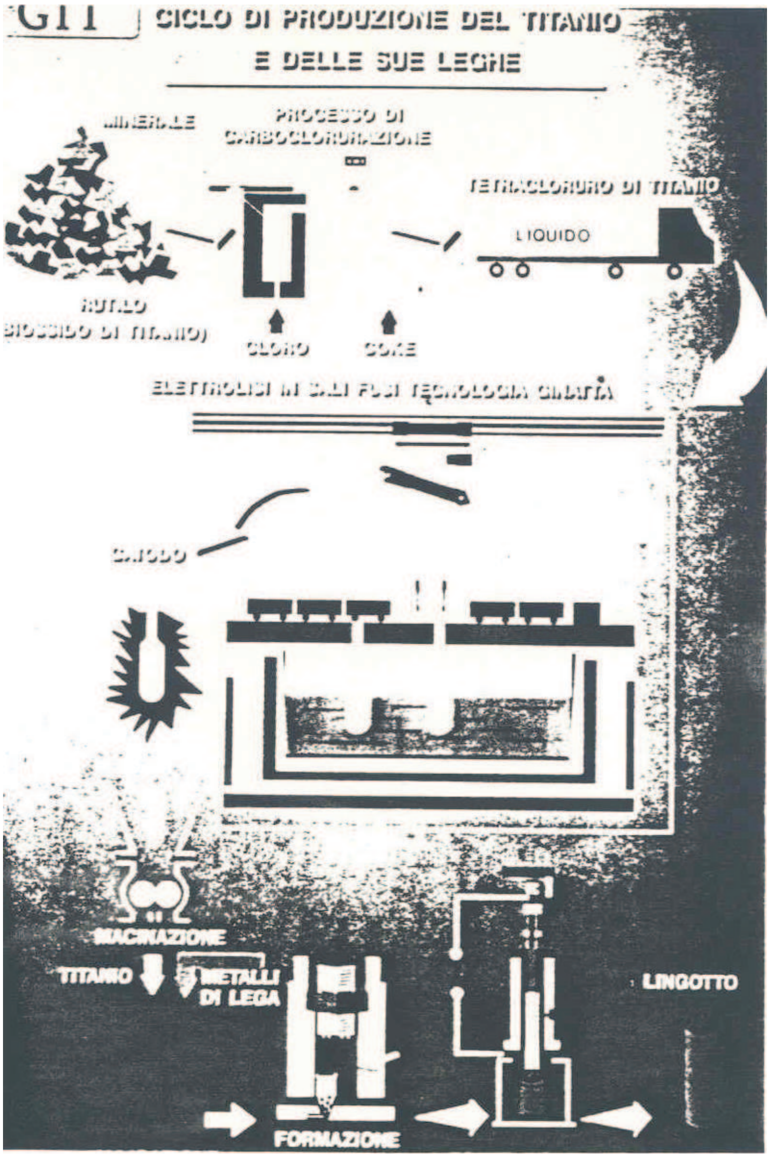

Fig. 3 - Ciclo di produzione di titanio e leghe (processo Ginatta)

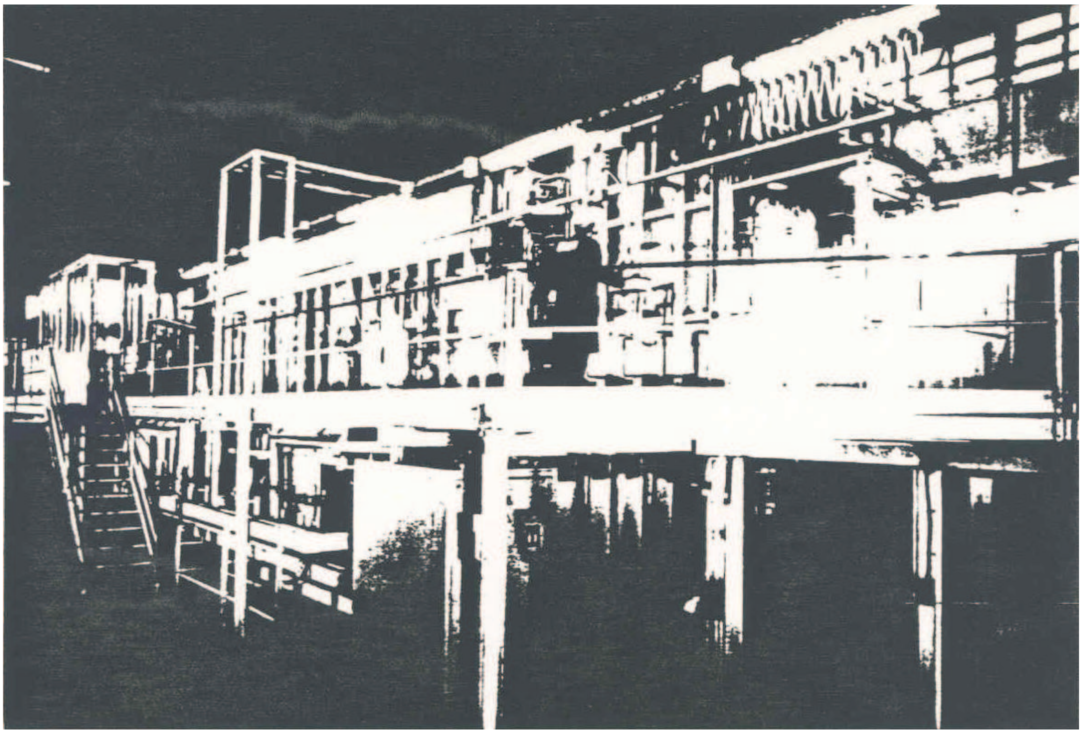

Fig. 4 - Impianto elettrolitico Modex III GTT a Santena (Torino)

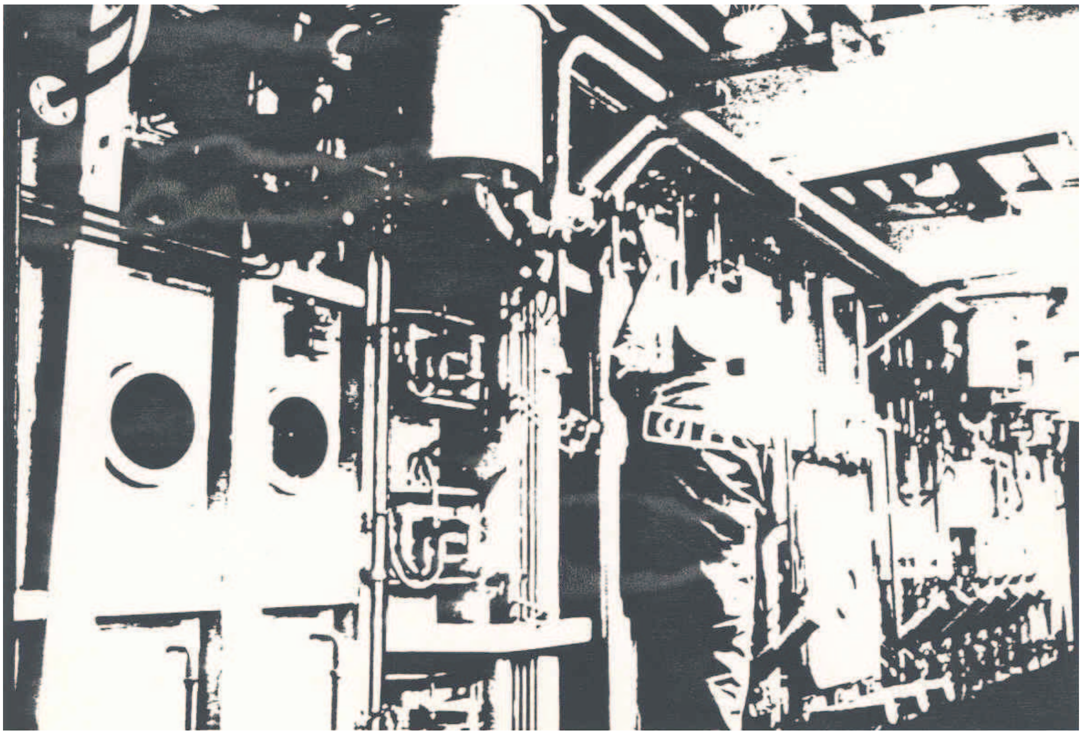

Fig. 5 - Impianto Modex III GTT, lato piping e strumentazione

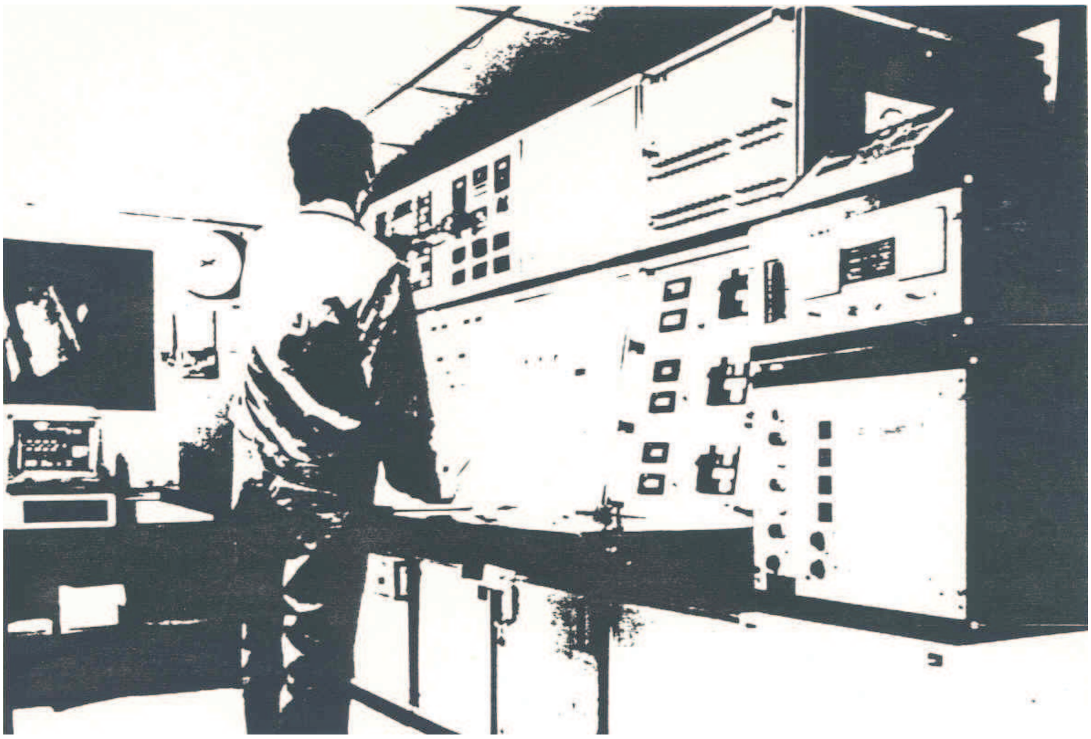

Fig. 6 - Impianto Modex III GTT, sala di controllo

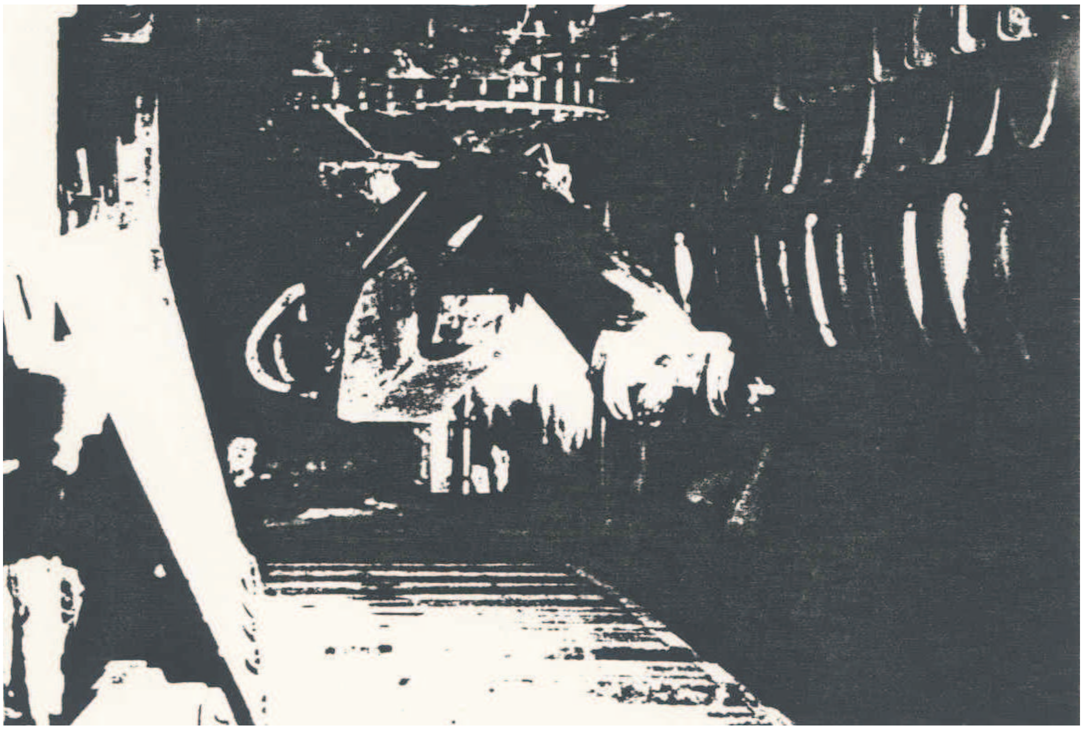

Fig. 7 - Impianto Modex III GTT, manipolatore per movimentazione elettrodi

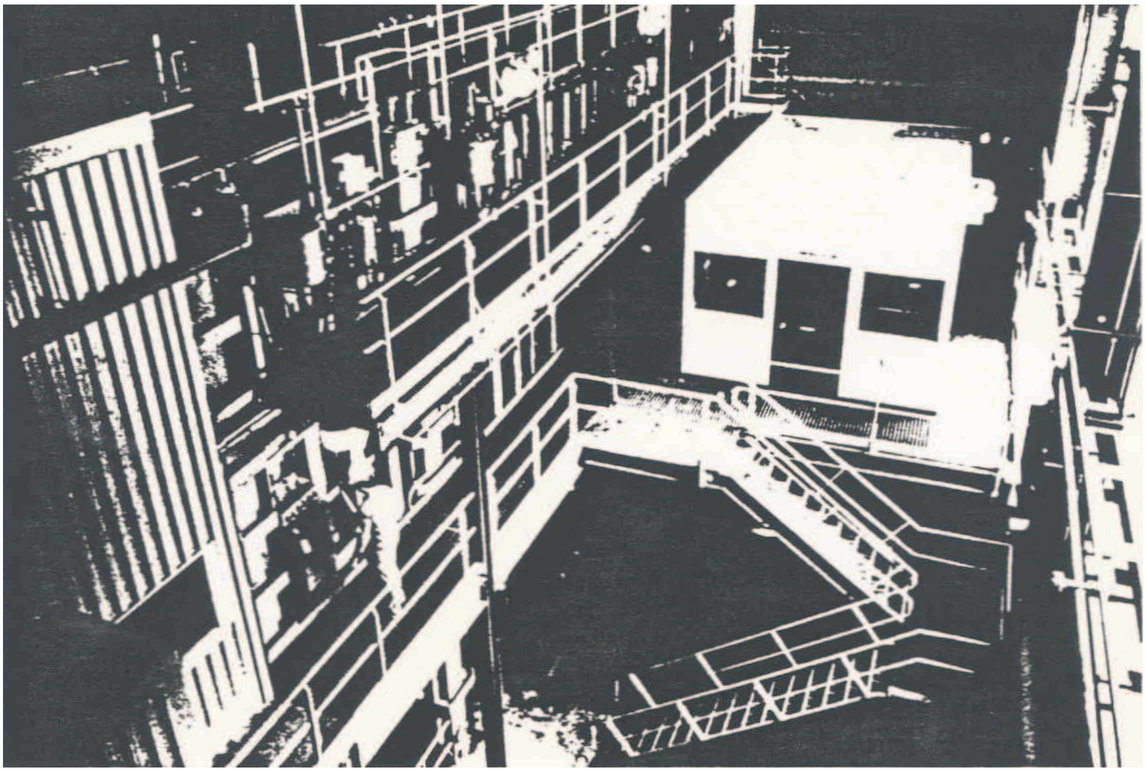

Fig. 8 - Impianto elettrochimico Modex IV RMI Co.
Ashtabula, Ohio (tecnologia Ginatta)

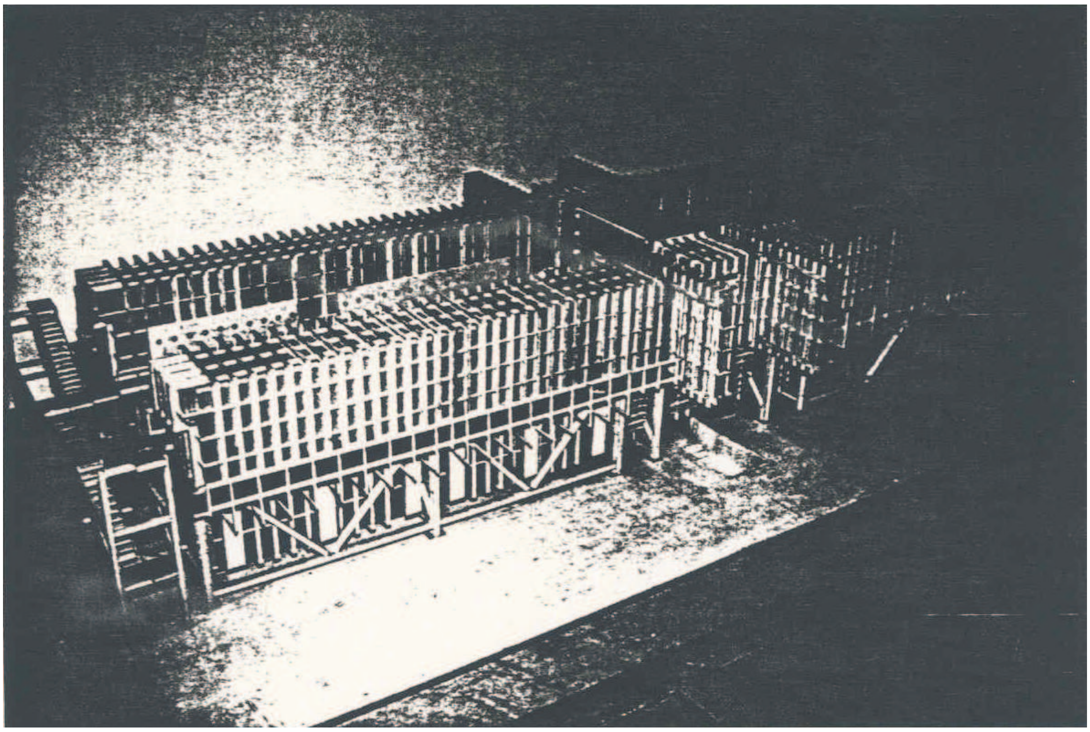

Fig. 9 - Impianto elettrolitico: modello di due moduli di 4 celle ciascuno

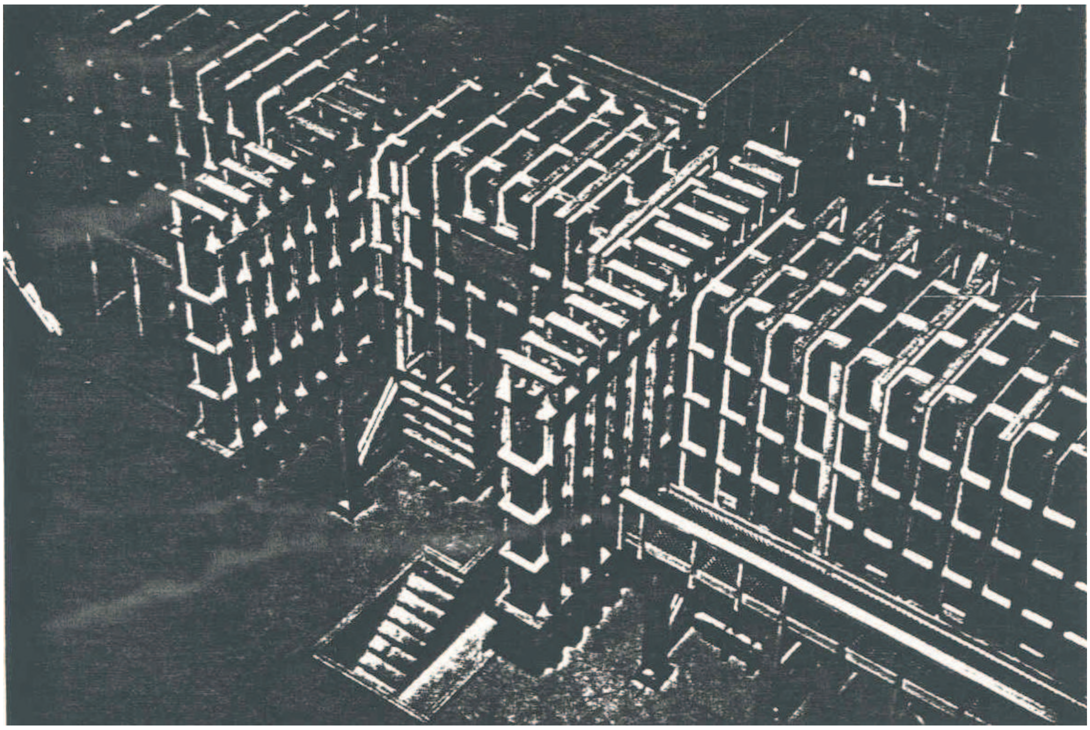

Fig. 10 - Impianto elettrolitico: precamera e stripper

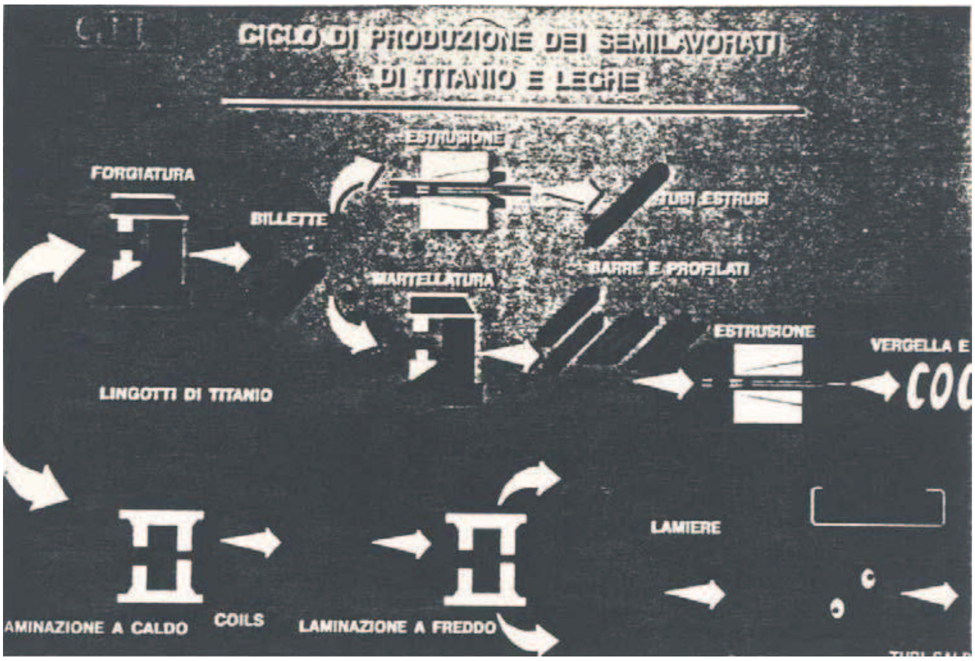

Fig. 11 - Produzione di semilavorati in titanio e leghe

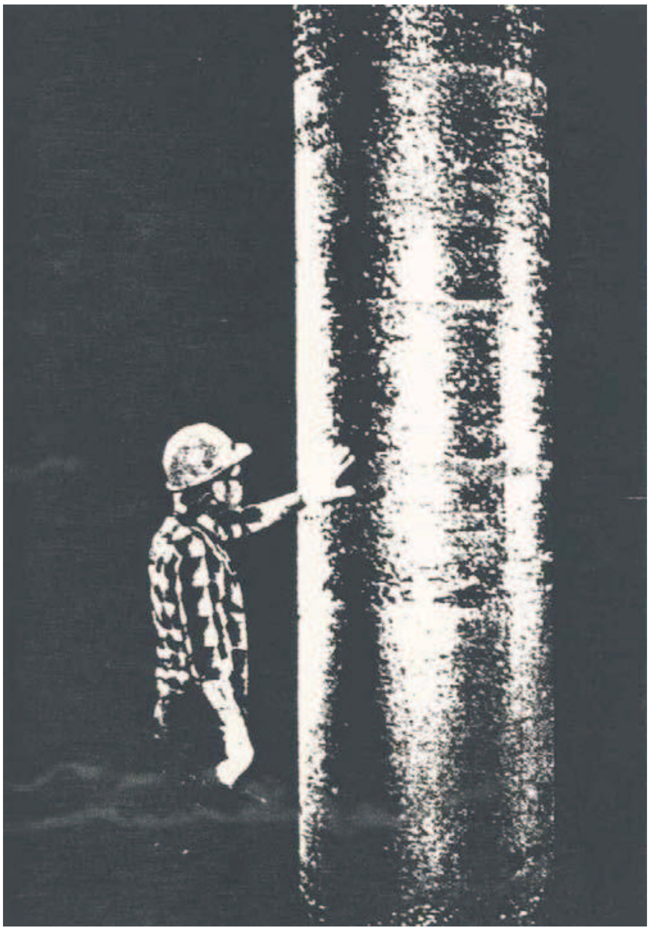

Fig. 12 - Lingotto di titanio ottenuto al VAR

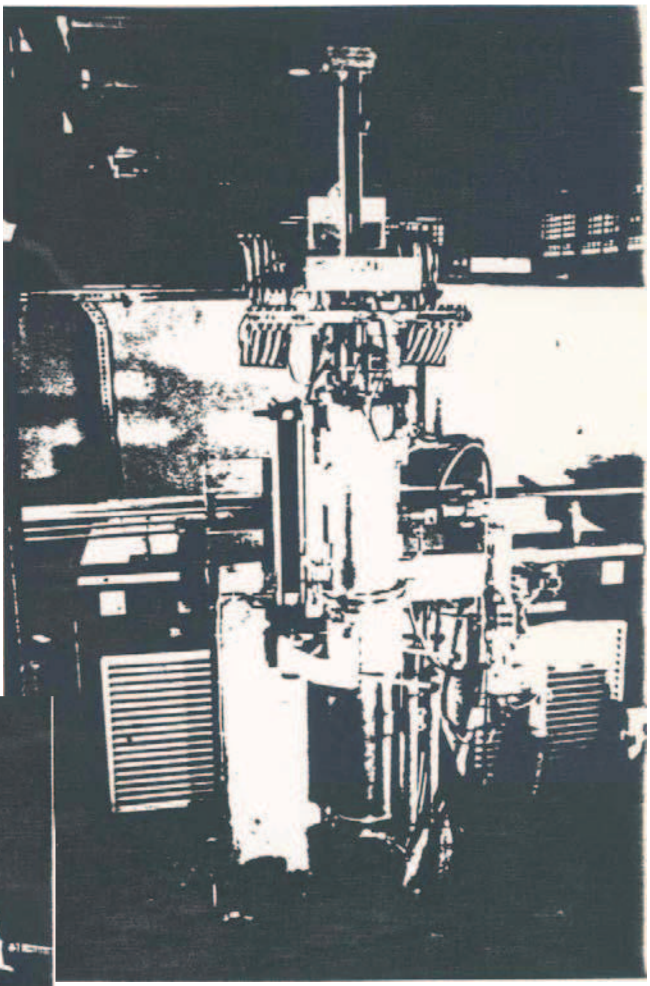

Fig. 13 -
Forno pilota VAR GTT, Santena

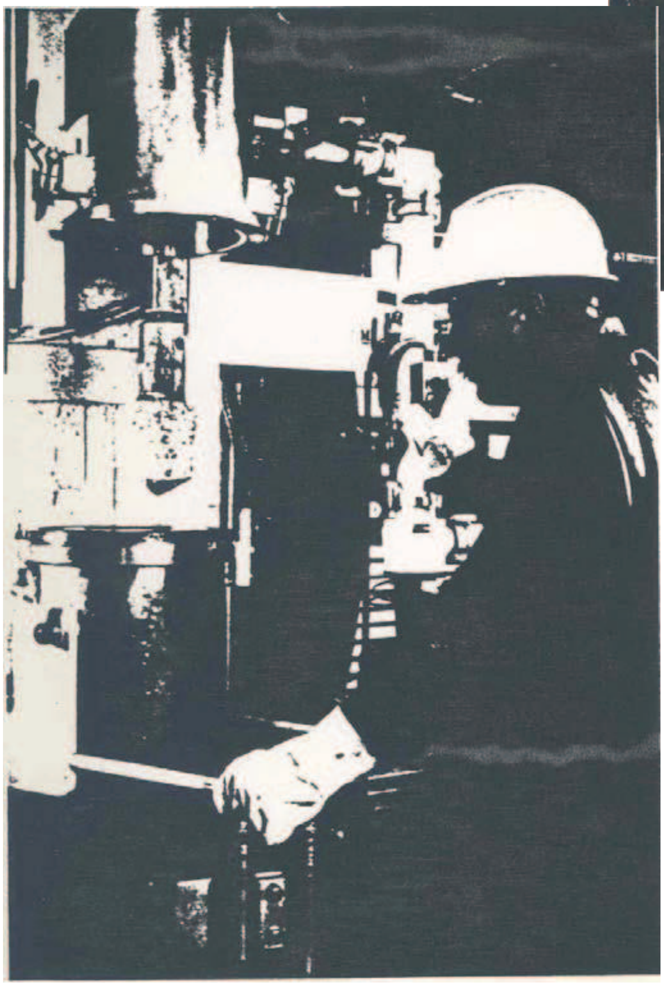

Fig. 14 - Forno
pilota VAR GTT, Santena:
crogiolo di fusione

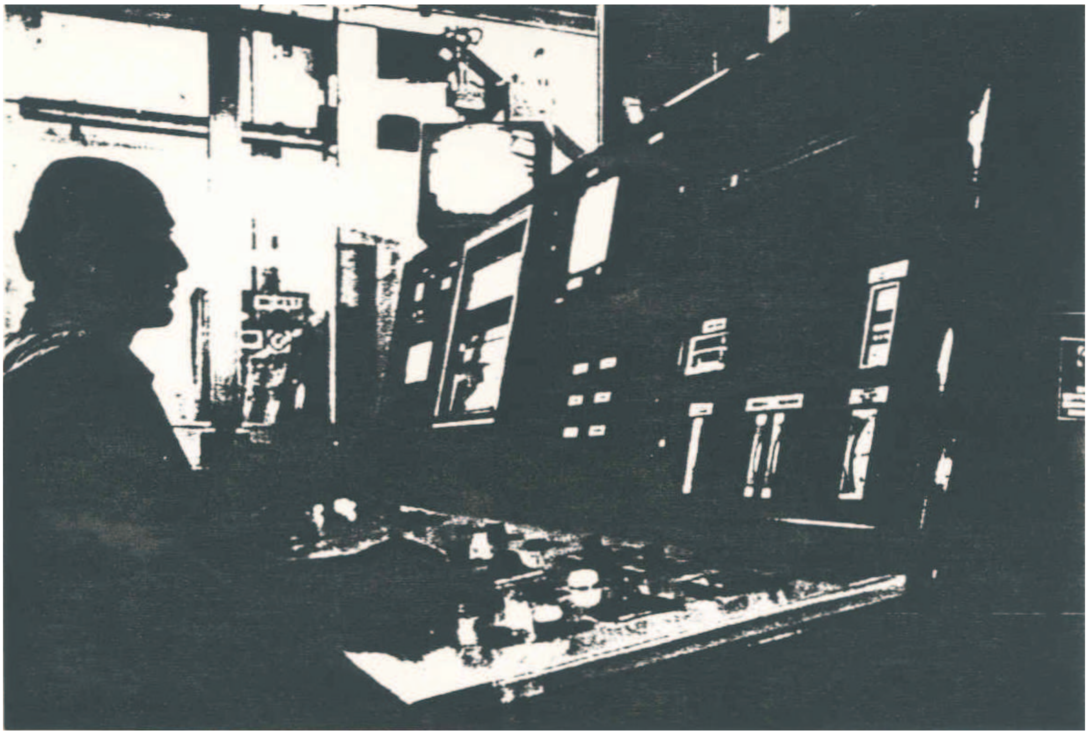

Fig. 15 - Forno pilota VAR GTT: cabina di conrollo

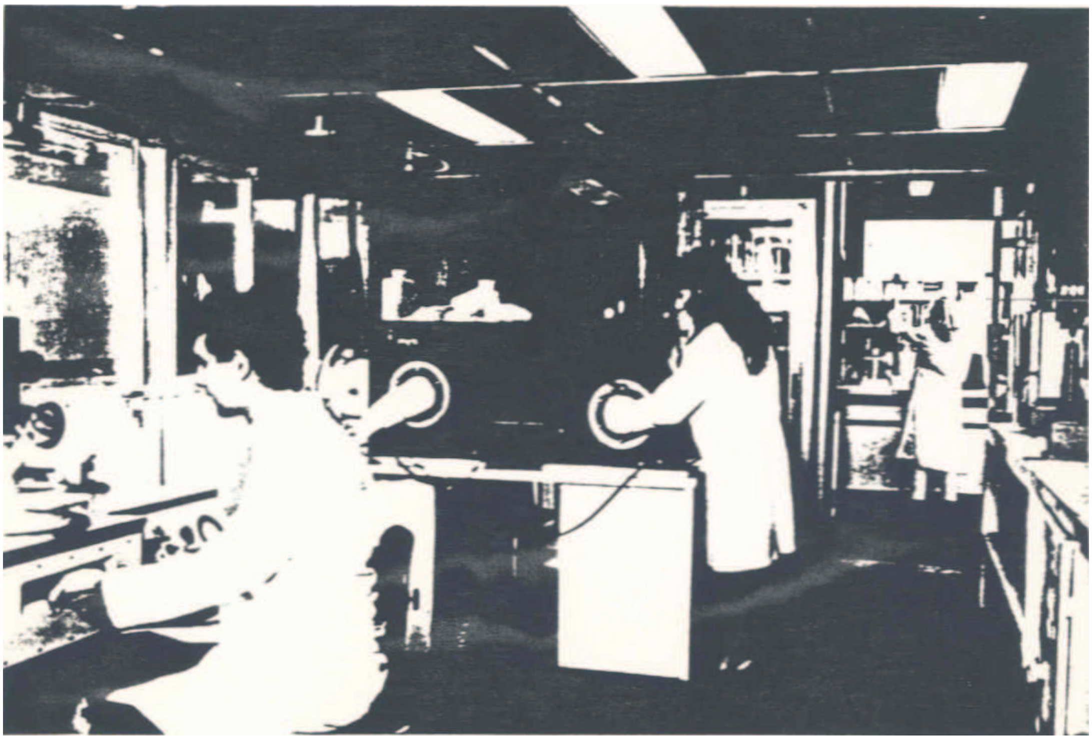

Fig. 16 - Laboratori GTT, Santena

Fig. 17 - Officina GTT, Santena: saldatura del titanio