NEW DEVELOPMENT IN TITANIUM ELABORATION-SPONGE, MELTING AND CASTING

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I. Introduction

During less than half a century since Dr. Kroll invented the extracting process of pure titanium from rutile ore and succeeded in its industrialization, accelerated research and developments on application of titanium, as well as on its refining and processing have made titanium one of the most indispensable materials, applied in many area from aerospace industries to more familiar area such as medical implant, leisure etc.

In this report, I would like to present a general view on the technical progresses of sponge, melting and casting.

II. Production of titanium sponge

1. The trend of the titanium sponge production in 1980's

Fig. II-1 shows the recent annual production of titanium sponge in Japan and U.S.A. In this figure, a drastic decline in 1982 and 1983, after a peak in 1981, clearly demonstrates that each maker could not help reducing its production in this period.

In 1984, however, the production of titanium sponge recovered by the following situations;

1) reduction of the excess inventory at the users

2) increase of new purchase of civil aeroplanes following to the aero industry's recovery

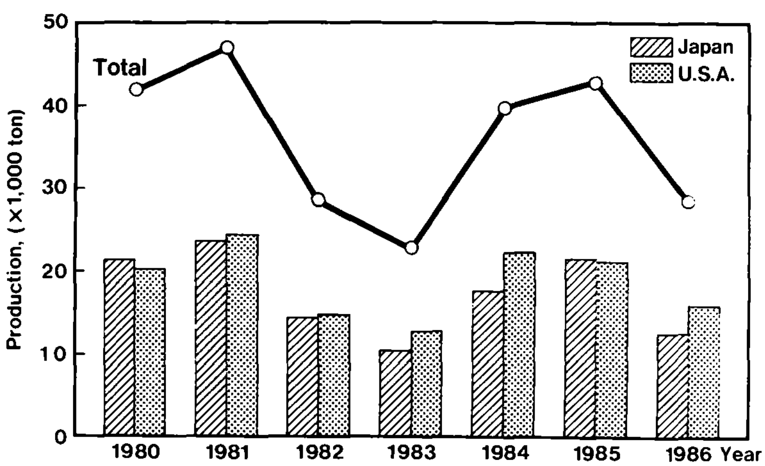


Fig.II-1 Titanium Sponge Production in Japan and U.S.A.

But in 1985, this upward trend could not continue. With a small production increase in Japan and U.S.A., the inventories in both countries began to increase largely.

In 1986, the titanium market declined again obliging the sponge makers to reduce their production drastically.

At present, since the latter half of 1987, the U.S. market seems to begin to recover and then the operating ratio of the U.S. sponge makers is rising.

2. Production methods for titanium sponge

2-1 Kroll process

More than 80% of titanium sponge is now industrially produced by means of Kroll process. Five companies in the Free World, USSR and China have been operating this process.

Showa Titanium Co., Japan, one of the latest comers, started operation of a 2,000 tons/year plant of Mg-reduction and vacuum distillation in Oct. 1983, the technical features of the plant are an integration of reduction and distillation, an enlarged unit (8 ∿ 10 tons) and adoption of the multipolar electrolytic cells for production of Mg.(1)

On the other hand, although International Titanium Inc., U.S.A., started its production in 1982 with the process of Mg-reduction and vacuum distillation, it announced to shut down its plant at the end of the year before last because of the declined titanium demand.(2)

At Toho Titanium Co., the reduction process with an inner case used in the reduction retort had been carried out separately from vacuum distillation. In 1980, they improved its process to an integrated one adopting inverted-U-type arrangement and increased its batch size from 1.5 ton to 4 ∿ 5 ton.(3) The following improved results are obtained;

1) increase furnace productivity by eliminating the inner case and cooling stage after reduction

2) reduce more than 40% of power consumption

3) reduce 40% of labour cost

4) reduce 20% of maintenance cost for reaction vessel

5) obtain more than 90% of yield to the class A sponge.

Osaka Titanium Co. reported the detailed recent progress in its Kroll process at the AIME TMS Annual Meeting held in Jan. 1988 at Phoenix, U.S.A.(4)

Above all, they emphasized;

1) At the $TiCl_4$ production stage, an operation of the fluidized-bed chlorinator at higher pressure increases its production rate and an operation at lower temperature precisely controlled by computer control improves the reactor lifetime and coke unit consumption (Table II-1).

2) At the reduction and distillation stages, the combined process and the enlargement of batch size (5 ∿ 10 tons) have increased the production rate (Table II-2) and contributed to great energy saving (Fig. II-2).

3) On the Mg electrolysis, the development of 100 kA multipolar cell has largely decreased power consumption making energy consumption of 9,500 kwh/ton of Mg Product be achieved. The yearly trend of its power consumption for production of Mg is shown in Fig. II-3.

Table. II-1 Ti Yield and Unit Consumption in $TiCl_4$ Production

	Fixed bed (1964)	FBR (1977)	FBR (Present)
Ti yield (%)	94.9	95.8	98.1
Consumption			
Coke (kg/$TiCl_4$ ton)	179	123	89
Cl_2 (kg/$TiCl_4$ ton)	879	811	797
Energy($\times 10^3$kcal/$TiCl_4$ ton)	1.563	1.056	500

Table. II-2 Batch Size and Production

Batch size	Produced Ti sponge (kg/batch)	Ti sponge production rate (in index)	Ti yield (%)	Vacuum separation rate (in index)	Total production rate (in index)
Non-combined process with inner case					
1.4 ton	1,400	1.0	97.0	1.0	1.0
2 tons	2,000	1.09	97.0	1.26	1.18
Direct and combined process*					
5 tons	5,700	2.76	99.8	2.48	3.28
7 tons	7,800	2.98	99.8	3.61	4.11
10 tons	10,300	3.53	99.8	3.81	4.61

* Retort without inner case.

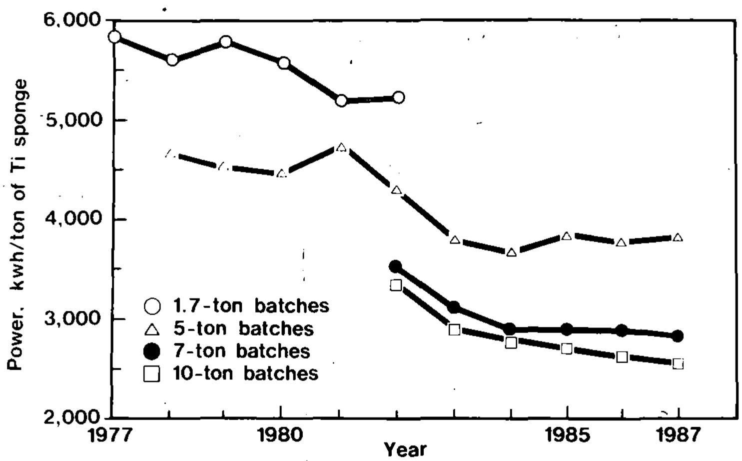


Fig. II-2 Reduction of Power Consumption in Increased Batch size

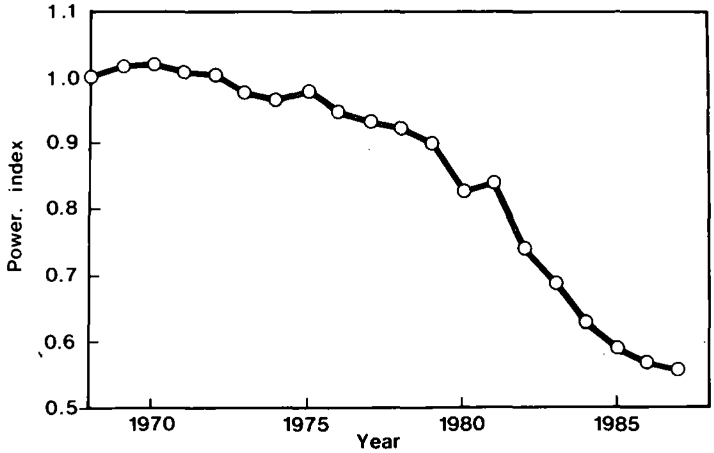


Fig. II-3 Reduction of Power Consumption in Electrolysis of $MgCl_2$

2-2 Hunter process

Deeside Titanium Inc., U.K., one of the three producers operating with Hunter process in the Free World, is reported to start up in Nov. 1982 its 5,000 tons/year plant as a replacement of shutdowned Titanium Plant, Imperial Chemical Industry.(5)

RMI Co. reported that the increased use of statistical process control systems and process improvements in the reduction and salt-metal separating areas have resulted in a significant reduction in the average oxygen content and a newly designed boring machine for the removal of salt and sponge from the reduction vessel has been successfully integrated into the process to replace existing chipping hammer.

2-3 New processes

(1) ALTI process

In the autumn of 1983, Albany Titanium Inc. announced its project to industrialize the titanium production process developed by Occidental Research Corp.(6) According to the patent, titanium can be separated from iron contained in ilmenite in the form of sodium fluorotitanate (Na_2TiF_5) obtained by adding sodium fluorosilicate (Na_2SiF_5) to ilmenite. The reduction of sodium fluorotitanate by Al-Zn alloy makes molten Ti-Zn alloy from which Zn is removed by evaporation.(7)

A.T. Inc. reported to have been developing this process under contract with U.S. Air Force, Army, and Navy and planning the construction of a commercial plant.(8)

This process is also suitable for powder production. It is reported that the powder of titanium alloy, for instance, containing Al and V, can be obtained by adding them into molten bath of Ti-Zn alloy and then evaporating Zn afterward.(9)

(2) Electrolytic process

Elettrochimica Marco Ginatta S.P.A., Italy, has been developing a new electrolytic process. According to the patent, it uses titanium tetrachloride or titanium oxide for the raw material, and chloride or fluoride for the salt of electrolytic bath. Adoption of heterogeneous bipolar electrodes of a fusible metal, such as lead, eliminates the diaphragm which causes various problems in the process.(10) It was reported that they licensed this technology to RMI Co. and USSR.(11)

3. High purity titanium

With the recent higher integration degree of the IC, a great attention has been paid to titanium for its electrode use replacing aluminum. To meet this requirement, high purity titanium has been developed.

Osaka Titanium Co. has delivered titanium of high purity, from 3-nine to 4-nine, obtained from the core of sponge cake in a large batch by the combined process using carefully refined raw materials.(12)

Toho Titanium Co. has also been preparing high purity grade of titanium represented as BHN73 (Typical value) by modifying conventional Kroll process.(3)

In the U.S., the ALTA Group, established in 1980, has constructed a production plant of capacity 4.5 tons/year of 4-nine titanium to meet the demand for electronics industry. It refines titanium sponge or titanium scrap electrolytically in the molten salt bath.(13)

Tosoh Co., makes titanium halide from commercial titanium of 3-nine in halogen gas, then refines and resolves it to obtain 5-nine titanium. It is reported to begin shipment of the sample.(14)

III. Titanium Melting

1. Consumable electrode vacuum arc melting

This process is dominant in titanium melting. The secondary melting rate now reached up to 2000 kg/h. Large ingot (max. 15tons, 1250mm dia.) with high quality has been available in practical use.(3)

Besides the movement toward larger ingot, many advances have been made in these years on automation of melting process and computer control of electrode positioning, melting speed, hot topping, stirring conditions, and vacuum level. It has become possible to print out an actual melt profile.(15)

Another improvement was directed toward homogeneity of large titanium ingots. Segregation of Fe and O in the ingot related to the secondary melting current pattern was explained by solidification pattern and equilibrium phase diagram. The secondary melting current pattern for these large ingots, including hot topping time which affects directly the productivity, should be decided by taking the customer specification into account.(16)

Further reduction of cost in this process will require a higher scrap ratio, side charge system(17) and adoption of rectangular ingot which can eliminate some of the succeeding processes.(18)

For the ß-type or near ß-type titanium alloys containing refractory metals of high density, now attracting attention, the solidification phenomena are under investigation and its result will be reflected to the quality of those material.

2. Non consumable electrode vacuum arc melting

Non consumable vacuum arc process has been used on industrial scale for melting of scrap and sponge. In this process scrap ratio is about 75% in average on account of oxygen content control.(19)

Retech Co. reported they have built NC rototrode arc melting furnace to accommodate ingot 800mm in dia. and up to 4500mm in length.(15)

Thyssen Edelstahlwerke AG's NC furnace, installed for the sake of lower cost and more flexibility in choice of raw materials, can cast ingots (max. 7tons, 700mm dia.) with melting rate of 400 to 800 kg/h.(19)

The analysis of the elements in the ingot cast in this furnace indicated that their fluctuation between the ingot's top and bottom was within the range of 0.2 wt% for Al and V respectively in Ti-6Al-4V and 0.02 wt% for O in CPTi, showing excellent homogeneity and good micro structure. Its mechanical properties was also comparable to that made by consumable electrode arc furnace.(19)

It is generally said that the material suffers from Cu contamination caused by slightly consumed electrode. But no problem is reported with slight increase of Cu to only 0.009%.(19)

However, this process requires a number of manual operations and produces a poor surface quality of the ingot because of a limited arc control. The improvement of surface quality will be studied in the future.

Although this process is applied exclusively for primary melting and the combination with VAR for the secondary melting is always required, it is still attractive from the viewpoint of utilizing titanium scrap in large quantity.

3. Electron beam melting

This process is mainly applied to making ingot from scrap by using hearth melting.

Hearth melting provides effective means for removing high density inclusions (HDI). This process can provide ingots in variety of shape, such as round and slab or even hollow. These have good surface quality in a single melting and are expected to eliminate some of the succeeding processes to reduce the cost.

There had been many investigations on the evaporation loss of Al in titanium alloy melting. The Al evaporation rate depends on surface temperature (i.e. beam power and scanning mode) and on liquid residence time.(20) Since the evaporation rate is so temperature-dependent, it is necessary to apply a very constant level of beam power and scanning programmed by computer in order to obtain a reproducible evaporation loss.(20)

A. Johnson Metals Corp. presented EBCHR (Electron Beam Cold Hearth Refining) process(21) with its examples of making pure titanium round ingot from 152mm dia. to 635mm dia. by 3200mm long, slabs up to 305t x 1118w x 3200ℓmm and hollow ingot.(22)

Recently, techniques of real-time composition monitoring with X-ray analysis equipment is reported to be available for this process.(23) Viking Metallurgical reported the melting of 610mm dia. x 4.6 tons of Ti-6Al-4V alloy electrode in 2400kw EB furnace into which processed scrap, sponge, 85-15Al-V master alloy and Al were charged. With homogeneous distribution of Al and V, the electrode was vacuum arc remelted into ingot which will meet the quality requirements of specifications such as AMS4928.(24)

Leybold AG showed a concept of multi-barstick continuous casting.(25) It will be expected further development of the equipment on its function. It also gives an expectation to the excellence in melting and refining of functional materials such as shape memory alloys and superconductive materials. With the further advance to programmed operation, much efforts are required for easier maintenance and lower equipment cost.

4. Plasma arc melting

Some plasma arc melting furnaces have been used for titanium primary melting for several years. R&D Institute of Retech, Inc., reported a plasma hearth furnace equipped with two guns supported by a ball joint system.(26)

As an example in U.S.A. Oremet Titanium's production unit installed in 1985 is presented in detail .(27)

The advantages of PA furnace compared with EB furnace are as follows;

1) No evaporation loss of alloy element is produced.

2) Calculated plasma rates in pound per hour are greater than electron beam rates at similar kwh input.

3) Unit construction costs are less than for EB furnace and maintenance is much less complex.

In an 600kw PASER (Plasma Arc Single-Electrode Remelt) furnace (Fig. III-1) supplied by Retech, Inc., plasma arc is generated by swirl flow hollow electrode and melting rate of 690 Kg/h is obtained. It has actually produced 450 tons of titanium alloy in this process which, in any case, must be followed by VAR melting.(27)

Daido Steel Co., presented 2 tons PPC (Plasma Progressive Casting) furnace aiming at elimination of primary VAR melting including compacting and welding to electrode.

Using six sets of plasma torch, ingot was melted into 440mm dia. x 3000mm and followed by VAR melting with the mechanical properties meeting ASTM and AMS specifications.(28)

Leybold AG installed a plasma melting test furnace with 650kw for R&D of titanium melting processes in 1985.

In the future, this process may be applied to powder making electrode, investment casting or Ti-Al intermetallic compound.

Improvement of the surface quality and the reduction of operating cost will be the main issues.

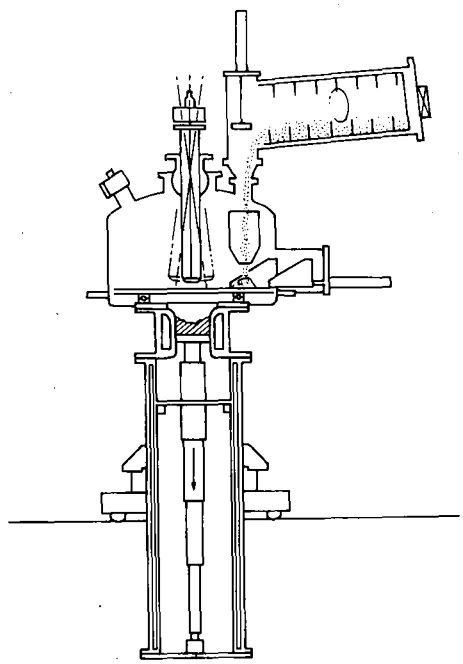


Fig.III-1 Schematic of PASER (Plasma arc Single-Electrode Remelt) furnace.

5. Recycle of scrap

The oil crisis and the expanded titanium use in aero and other market raised sponge prices and urged imminent investigations for recycle of scrap.(29) The scrap ratio for ingot melting is 30 to 40% in Europe and USA and 15% in Japan.

In general, swarf is possible to be mixed in sponge compact up to 50%, crop can be used in constructing electrode up to 80%.(32)

AMS specification now admits using processed scrap in melting Ti-alloy for the aero use on condition that X-ray inspection verifies no HDI.

The cost efficiency of titanium scrap depends on sponge prices and the cost of recycling and processing. Some cases of utilization of titanium scrap, lately reported, are introduced below.

Schmiedewerke Krupp Klockner GmbH, and Messerschmitt Bolkow-Blohm GmbH, West Germany, reported the results of VAR melting of Ti-6Al-4V ingot using chip mixed to 50%.(30) They said that no problem was found in the mechanical properties, micro structure and ultrasonic test and that no HDI was detected X-ray inspection. At the same time, Messerschmitt Bolkow-Blohm GmbH, confirmed no difference in the fatigue strength between the materials 50% chip mixed and no scrap used.(31)

Vereinigte Edelstahlwerke AG. tested helicopter rotor made at more than 50% Ti-6Al-4V scrap ratio; JT9D fan blade made at 100% and other engine disk also made with scrap. Good mechanical properties were reported on all of them.(32)

For further cost reduction of titanium alloy, besides lowering recycle and processing cost, as mentioned above, it is most important to establish an effective classification system for all sorts of scrap in cooperation with aero plane and engine makers to take advantage of scrap mixing.

IV. Titanium casting

1. General situation of titanium casting

Forgings so far have been dominantly used for aero parts, but with lower yield and higher cost. Among the ways recently searched for reduction of cost, castings are paid great attention because of its near net shape.

The demand for titanium castings has got a steep increase(33), as shown in Fig. IV-1 over the technical difficulties caused by the high reactivity of the material in its molten state. This is due to the fact that the castings have acquired a comparable qualities to the forgings favoured by recent technical advances.(34)

A compressor case, even in the field of aero parts requiring high performance, has been made in the size of more than 1000mm in dia. and more than 100kg in weight by means of investment casting for use of engine.(35) And also, titanium castings were selected to be used for the intermediate case of V2500, a new typed engine jointly developed by five countries.

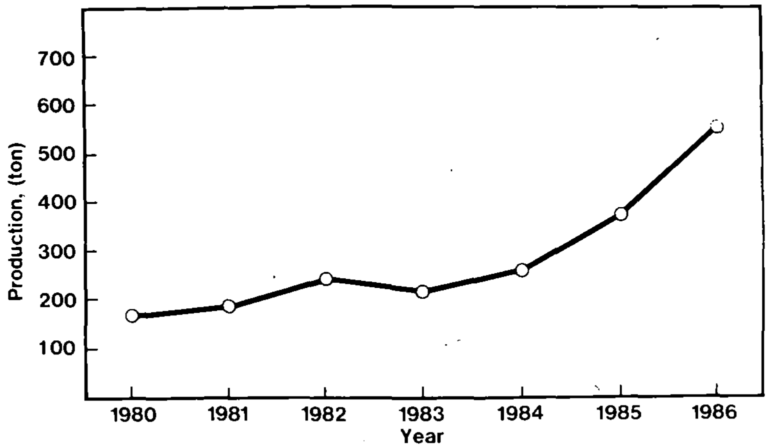


Fig. IV-1 Trend of Titanium Casting Production in U.S.A.

2. Casting procedure

2-1 Casting equipment

Fig. IV-2 shows a concept of casting equipment. Although consumable electrode arc melting is the most common, electron beam, plasma beam and induction are also partly employed. The molten metal stays in water cooled tiltable crucible, in order to have HDI separated, and accumulate to a certain amount sufficient to casting into mould. Casting of large or precise parts is often carried out centrifugally. A latest commercialized large scale equipment produces castings of up to 1000kg in total weight with fully automated operation from melting to casting.

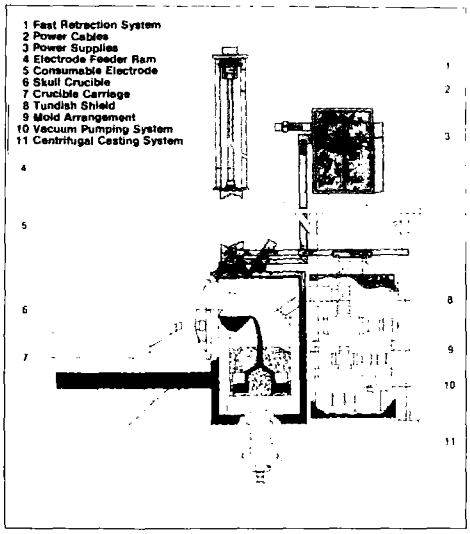


Fig.IV-2 Casting Equipment Combined with Consumable Electrode arc Furnace (Courtesy of LEYBOLD AG)

2-2 Titanium alloys used for castings

In case of titanium alloy casting, though Ti-6Al-4V is the most common, castings of ß alloys such as Ti-15-3, ßc and other alloys appropriate for castings have been investigated and expected promising.(36)

2-3 Kinds of mould

There are several kinds of mould;

(1) investment mould
(2) rammed graphite mould
(3) ceramic mould
(4) sand mould

Investment and rammed graphite have been actually used. The former is employed for aero parts requiring high performance, and the latter for larger parts such as chemical or marine use.

In the future, investment casting will gain dominance due to the strong demands for higher quality and the possibility of mass production and process automation. Ceramic and sand were also developed and partly used in the production. Sand mould may be expected promising in cost reduction.(37)

3. The quality of casting and examples of application

The products as cast contain porosities and have a lower fatigue strength with wide fluctuation. However, for important parts, such as aero parts, those defects can be overcome by HIP and an appropriate heat treatment to obtain a quality close to that of wrought ß annealed material.(38, 39, 40) When the corrosion resistance is mainly required, in such a marine or chemical industry, castings are often used in as cast.

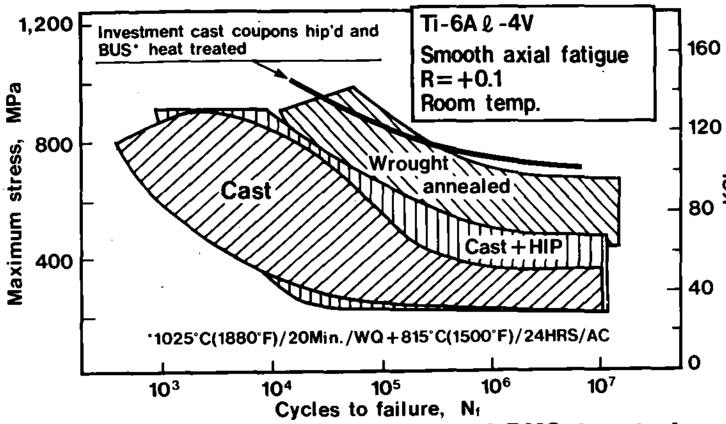
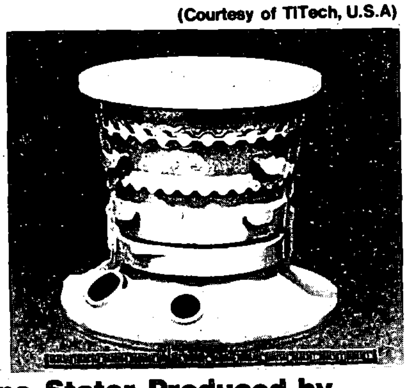


Fig.Ⅳ-3 Fatigue life Comparison of BUS treated HIP'd Investment Cast Coupons with Annealed Wrought, Cast, and Cast+HIP Material. (40)

Examples of Application

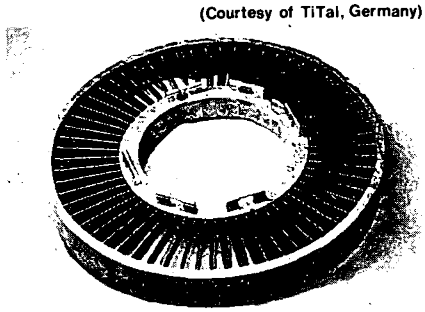
T-700 Gas Turbine Engine Compressor Case Produced by Investment Casting

(Courtesy of TiTech, U.S.A)



Jet Engine Stator Produced by Investment Casting (A Wall Thickness 2mm, and Diameter of 580mm)

(Courtesy of TiTal, Germany)



4. Prospects for the future issues

The demands for titanium castings in the U.S. have increased at a rate of more than 20% a year in average during from 1980 to 1986,(33) and this tendency will continue. According to a certain aero engine maker, the weight ratio of castings for a gas turbine will amount to 16% in 1994, compared with 6% at present.(33) Wider applications and demands for titanium castings are expected in many fields, such as marine, chemical industry and medical implant.

Present technical issues to be solved are;

(1) development of suitable alloys for castings

(2) establishing the optimum conditions of HIP and heat treatment for improved mechanical properties

(3) reduction of cost through technical development and application of sand mould

V. Conclusion

Sponge, melting and casting of titanium were reviewed above on their recent situation and important issues.

Summary;

1. Although the basic production process of titanium sponge has not yet changed, lots of technical advancement has been achieved.

While the Kroll process or Hunter process will continue to be the basic methods. Some new methods have been tried to industrialize and expected promising.

2. In melting, while CE/VAR is still dominant, applications of EB or PA furnaces, enlargement of melting size and advancement of scrap recycle shall be considered to meet the various needs and cost reduction.

3. Casting has promising technical potentialities for not only aero use but also chemical or medical use. The advanced technology can give complicated shapes in near net or net shape and competitive properties to conventional forgings.

Above all, the effect of HIP and heat treatment should not be overlooked.

Acknowledgment

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References

(1) The rare metal news, Jan. 8, 1984

(2) American Metal Market, Dec. 29, 1986

(3) S. Okudaira, Metallurgical Review of MMIJ, Vol. 4, No. 1, 1987

(4) T. Noda, TMS Light Metals Committee at the 117th TMS Annual Meeting

(5) D. Smith, The 5th International Conference on Titanium, 1984

(6) American Metal Market, Oct. 21, 1983

(7) P. A. Hard, et al., USP 4390365, 1983

(8) American Metal Market, May 28, 1987

(9) US Patent 4602947, 1986

(10) M. V. Ginatta, USP 4400247, 1983

(11) American Metal Market, Jan. 26, 1988

(12) J. Iseki et al., International Conference TDA, 1986

(13) American Metal Market, July 24, 1985

(14) NEW MATERIAL PRESS, April 15, 1986

(15) M. Schlienger, The 5th International Conference on Titanium, 1984

(16) H. Shiraishi, et al., The 5th International Conference on Titanium, 1984

(17) H. Kusamichi, et al., "High Efficiency Melting Process for Large Titanium Ingot" Proc. 7th ICVM, 1982, Tokyo, Japan

(18) H. Ichihashi, et al., Journal of The Iron and Steel Institute of Japan, Sept., 1986

(19) K. Rüdinger, et al., The 5th International Conference on Titanium, 1984

(20) A. Mitchell et al., The 5th International Conference on Titanium, 1984

(21) Howard R. Harker, et al., International Conference TDA, 1986

(22) William C. Acton, American Metal Market, Nov. 4, 1987

(23) A. Mitchell, University of British Columbia, J. Colby, KEVEX Corporation, E/B Conference, 1987 USA

(24) W. E. Herman, et al., International Conference TDA, 1986

(25) W. Dietrich, et al., The 5th International Conference on Titanium, 1984

(26) M. P. Schlienger, et al., International Conference TDA, 1986

(27) S. Stocks, et al., International Conference TDA, 1986

(28) T. Yajima, et al., International Conference TDA, 1986

(29) K. Rüdinger, The 5th International Conference on Titanium, 1984

(30) K. H. Kramer, et al., The 5th International Conference on Titanium, 1984

(31) J. Berggreen, The 5th International Conference on Titanium, 1984

(32) H. Jaeger, et al., The 5th International Conference on Titanium, 1984

(33) Ward W. Minkler, International Conference TDA, 1986

(34) W. J. Barice, Titanium Net Shape Technology, 1984

(35) C. Ellebrecht et al., The 5th International Conference on Titanium, 1984

(36) R. R. Boyer, National SAMPE Technical Conference, Vol. 17, 1985

(37) Mihin Sen, Dy, International Conference TDA, 1986

(38) J. Kopchik et al., Proceedings Annual Forum of the American Helicopter Society Vol. 41, 1985

(39) D. Eylon et al., SAMPE Journal, Vol. 22, 1986

(40) D. Eylon et al., The 5th International Conference on Titanium, 1984