Overview of Emerging Titanium Technologies

Edwin H. Kraft, Principal

EHKTechnologies

Vancouver, WA

Success Strategy for Advanced Materials Ventures[SM]

Good Morning.

I intended to present an overview of emerging technologies in many areas of titanium. However, time constraints required that I focus on providing an updated overview of the emerging extraction technologies. There remain just over 20 activities around the world seeking to provide lower cost through new extraction methods. In recent discussions with most of these developers, I have gained new information and insight into the processes and their status, which I would like to share with you.

In Memory

This Presentation is Dedicated to the Fond Memory of

Dr. Sidney Diamond

His Curiosity Knew No Bounds

Born Jan. 6, 1933

BS Met. Engg. MIT

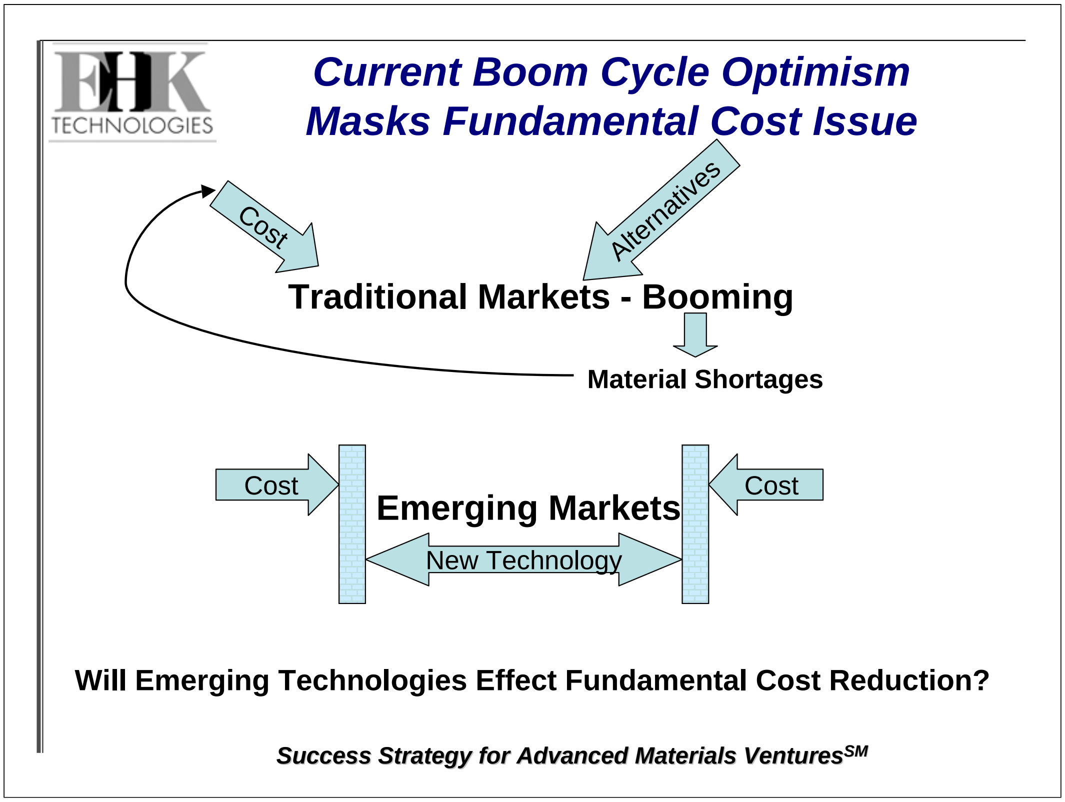
Ph.D. U. Illinois

US Steel, Westinghouse, Battelle Columbus

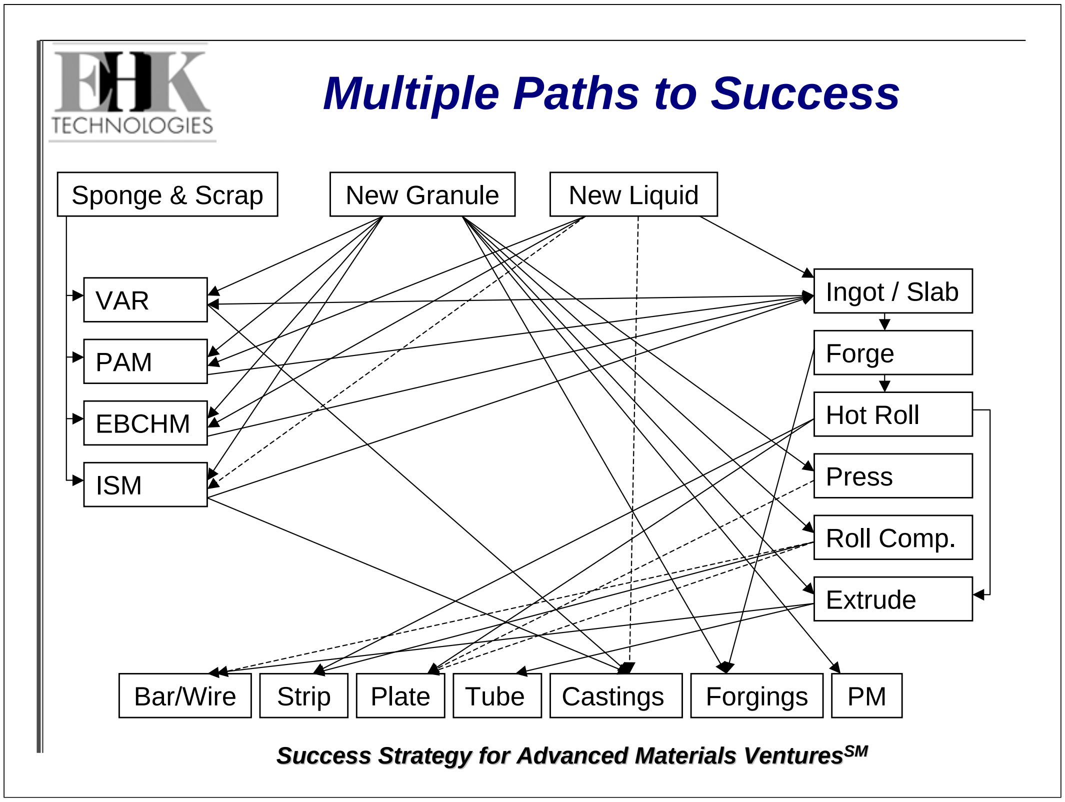
DOE: Sr. Technology Mgr.
- **80mpg Car**
- **Malleable Ceramics**
- **Fuel Ionization**
- **Champion For Titanium**

Inspiration & Encouragement To All He Encountered

I hope that many of you had the exquisite pleasure, as I did, of knowing Dr. Sid Diamond of DOE. Unfortunately we recently and unexpectedly lost Sid. I am dedicating this presentation to Sid in recognition of his championship of the cause of titanium applications in transportation. Sid's curiosity truly knew no bounds. I and many of you will certainly miss his encouragement of new ideas, his inspiration, his smile and his friendship.



It is no secret that we are currently well into a boom cycle in the business of titanium. Stories abound about tight supplies, long deliveries and high prices. It is also no secret that all past boom cycles have ended and the industry returned to tough times with no significant long term growth. There is optimism that “This time will be Different!”. However, this optimism may mask attention to the fundamental cost issues that have blocked expansion of emerging markets. The new technologies we will look at suggest the promise of lower cost to remove this blockage. There is very encouraging progress toward answering the question of whether these technologies will effect fundamental cost reduction.



I have divided this summary into those processes that promise to produce liquid and those that expect to produce granular or powder titanium. This diagram is intended to show that there are numerous paths that either of these forms may take to provide new or traditional titanium products.

Emerging Process Technologies

- **Melt Technologies: Not New, But Improving / Expanding**
  - **Cold Hearth Melting – Increasing Acceptance**
    - **Electron Beam**
    - **Plasma**
  - **Electroslag Remelt ?**
  - **Induction Skull Melting – In-Situ Alloying Development**
- **Emerging Ti Extraction Technologies** ← This Presentation
  - **Liquid Product**
  - **Solid Product**

  Ref: ORNL/Sub/4000023694/1; http://www.ms.ornl.gov/programs/energyeff/HVPM/default.htm
- **Developing Powder/Granule Consolidation Methods**
  - **Roll Compaction, Press Etc.**

Success Strategy for Advanced Materials Ventures[SM]

I would be remiss if I did not point out that there are significant advancements in traditional melt technologies which are improving the quality and reducing the cost of Ti products. Likewise, there is beginning effort to take the powder products of the new extraction technologies and consolidate and further process them into lower cost and in some cases new products. The key to this potential success however, still lies in commercialization and truly lower Price of the new extraction products.

Emerging Ti Extraction Technologies

EHK TECHNOLOGIES

Processes Producing Liquid Ti

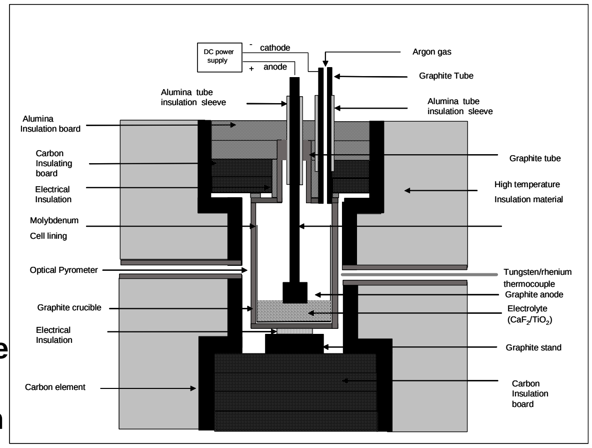
- **Issues:**
  - **Can it co-reduce alloy precursors or add alloy elements?**
  - **Purity: LDI/HDI, O_2 level control, other contaminants?**
  - **Can it be used as feedstream for PAM?**
  - **Mechanism for tapping / casting?**
  - **Cost?**
- **Candidate Processes:**
  - **CSIR**
  - **DMR**
  - **Ginatta**
  - **MIT**
  - **QIT / Rio Tinto**
  - **Tresis**
  - **[Dynamet Technology Low Cost Feedstock]**

Success Strategy for Advanced Materials Ventures SM

We will first look at the processes aimed at producing lower cost liquid titanium or alloy that can be cast either into ingot or billet or near net components. Some of the issues I have discussed with these developers are listed here. The answers are not yet clear in many cases. The list we will address contains some well known efforts and some less familiar.

CSIR – S. Africa

- Initial Experiments: Electrolysis of TiO_2 in CaF_2 Electrolyte
- 6% to 20% TiO_2 Operated @ 1750 - 1800°C
- Intended Product: Ti Liquid for Casting
- High C: Ti / C = 2
- Status: TiO Produced
- Future Work: Test Various Electrolytes & Use OS Technique For O Reduction. Anode – Cathode Spacing & Inert Anode For C Reduction; Achieve Ti Production



Ref.: van Vuuren et al; submitted to JOM

Success Strategy for Advanced Materials Ventures[SM]

CSIR is the largest Government and industry directed scientific and technological R & D and implementation organization in Africa and currently conducts about 10 % of all R&D work on the continent. One key goal is to increase the added value of the Ti mineral resources in Southern Africa. In addition to investigating the potential of processes being developed by others, they have an active project to develop an electrolytic process to produce liquid Ti for casting. Initial work showed some progress, and the need for additional effort to achieve Ti production.

EHK TECHNOLOGIES

DMR

- “Enhanced Aluminothermic” Process
- No Halogen Involvement
- Rutile Feedstock
- Ti or Ti-6Al-4V Liquid Product
- “Standard Process Equipment” Intended for Economical Broad Casting Applications
- Patent Application in Process
- Laboratory Testing Continues

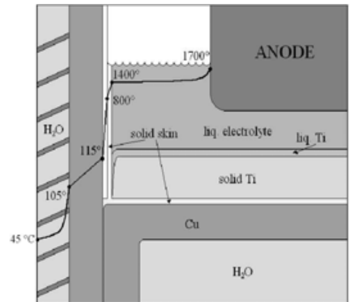
Success Strategy for Advanced Materials Ventures^{SM}

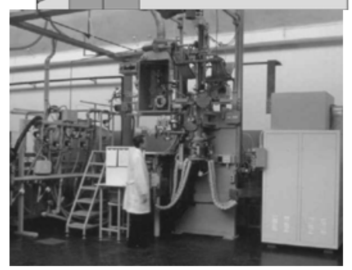
DMR is a small company in the Eastern US that has developed an “enhanced aluminothermic” process to convert TiO_2 into liquid Ti or alloy. As they are still in the patent application process, they cannot disclose details. However, they claim to use no halogens, and to use available and standard process equipment. Their intention is for broad application in the casting industry – perhaps, if my understanding is correct, analogous to the aluminum die casting industry.

EHK TECHNOLOGIES

Ginatta

- **Electrolytic Reduction of $TiCl_4$ In "Multilayer Cathode"**
- **Cathode Phase Consists of K, Ca, Ti Halides & K, Ca**
- **Liquid Solidified Into Ingot or Slab**
- **Current Pilot Plant Offering CP and Alloy Ingot, 130 – 250 mm Diameter**
- **Currently In "Discussions"; No New Information Available**





Ref.: Ti-2003, Hamburg

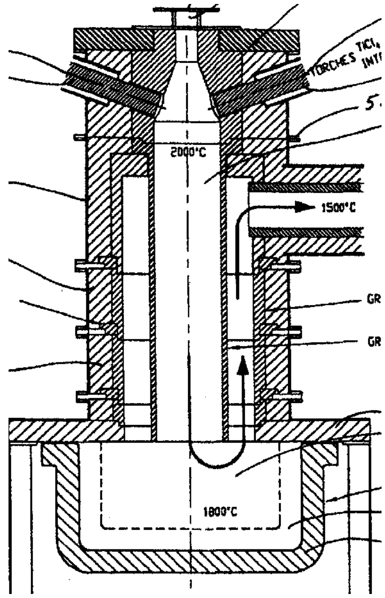
Success Strategy for Advanced Materials Ventures SM

Dr. Ginatta certainly deserves the dedication award for his perseverance in development of his electrolytic process for Ti liquid and billet casting. His website is currently offering CP and alloy ingot for sale, I assume from his process. In recent communication he was not able to offer current status due to discussions with what I took to be other collaborative parties.

EHK TECHNOLOGIES

Tresis

- **Argon Plasma Reduction of $TiCl_4$ with Mg (or Na)**
- **Based on Pilot Plant Work in 80's @ JPL on Si Production**
- **An Analysis of Ti Patent & Process Indicated Feasibility & Projected Cost for Ingot of ~$4.66 (Ti) to ~$6.16 (Ti64) If Integrated w/ PAM**



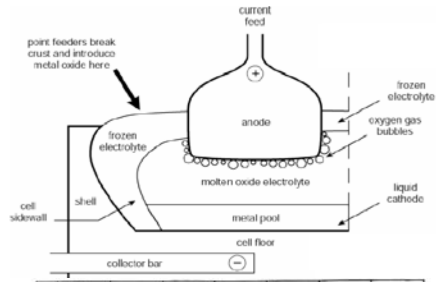
Success Strategy for Advanced Materials Ventures [SM]

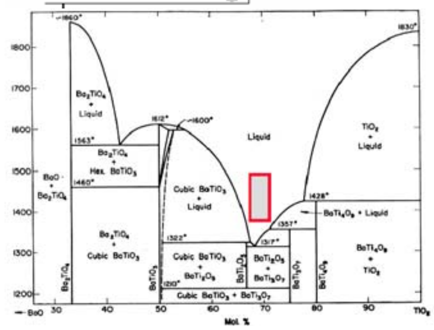
Tresis International has patented a process for the argon plasma reduction of $TiCl_4$ by Mg or Na. It is patterned after a JPL developed process for Si production in the 80's. A very thorough techno-economic analysis was performed a few years ago, which indicated feasibility and attractive costs. It is interesting as either a stand alone process or as a front end to PAM processing. Projected cost (not price) with PAM was $4.66 for "CP" to $6.16/lb for Ti-6Al-4V ingot.

TECHNOLOGIES

MIT Two-year Titanium Initiative

- **Liquid titanium by electrolysis of TiO_2 in an oxide melt**
- **Sadoway Process to develop new Ti-3Fe-1Nb alloy for low-cost armor-grade titanium @ $2.50/lb**
- **electrical conductivity and transference number measurements performed**
- **electrolysis of TiO_2 – BaO at 1500° with molten Cu cathode confirmed oxygen evolution on idealized anode**
- **bench-scale experiments in progress for process parameter limits, scaling, anode selection**



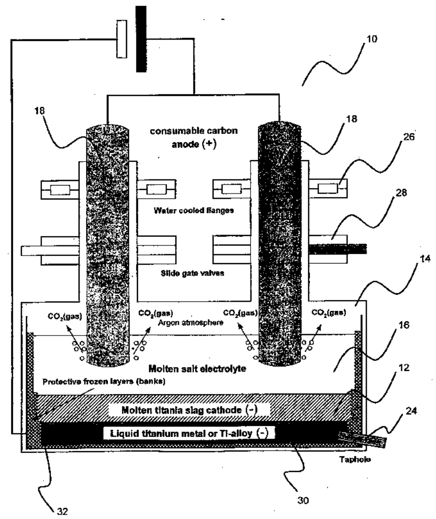


Success Strategy for Advanced Materials Ventures[SM]

Professor Sadoway at MIT has launched a two year initiative to demonstrate electrolysis of TiO_2 in an oxide melt analogous to aluminum production. One near term objective is production of armor grade alloy at a cost (again, not price) of around $2.50 / lb. Much of the basic measurements have been done and bench scale experimentation is underway.

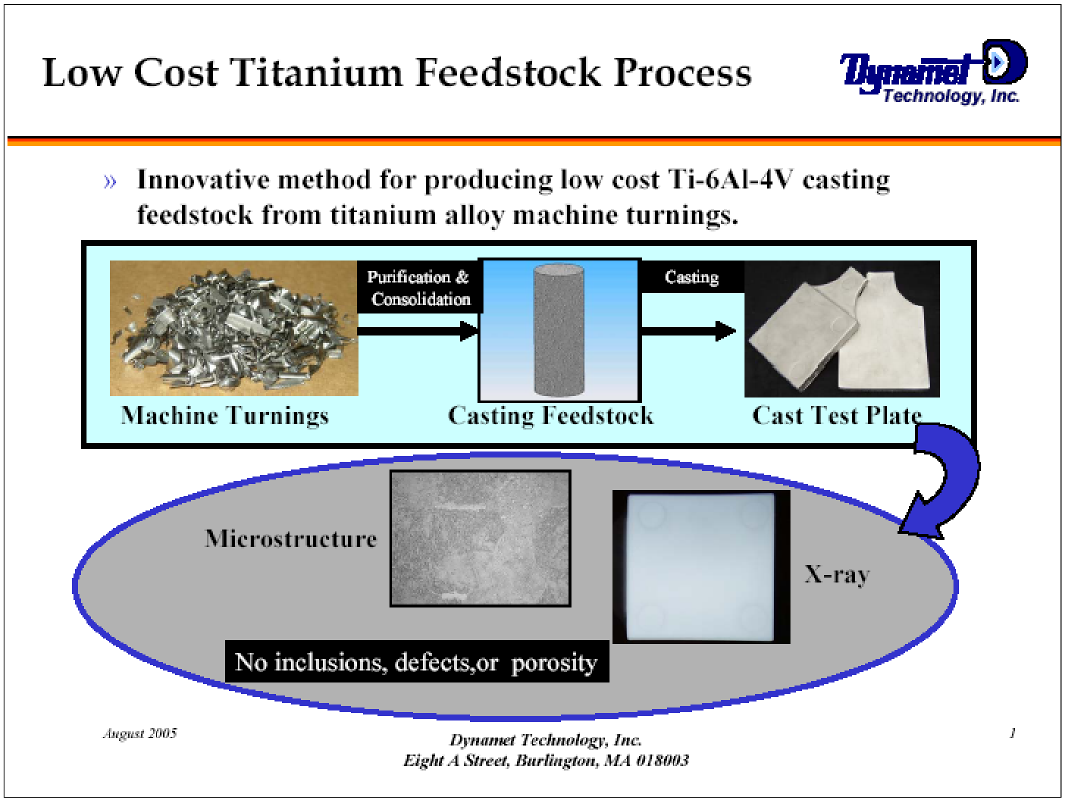
Quebec Fe & Ti / Rio Tinto

- Information Based on Int'l Patent Appl. WO 03/046258 A2
- Slag Electrolysis
- Containment by Frozen Slag, Electrolyte and Ti
- Multiple Variations of Anode, Electrolyte (e.g. CaF_2) & Operation Method
  - Ex. 1: Molten CaF_2 & Ti Slag; Step 1, Electrolytic Removal of Fe, Cr, Mn etc. Impurities; Step 2, Electrolysis for Ti
  - Ex. 2: Single Step Electrolysis of Low Impurity Upgraded Slag
- Status: Still Proceeding; No New Information



Success Strategy for Advanced Materials Ventures[SM]

I have reported previously on the QIT effort at electrolysis of titanium slags obtained from their Ilmenite processing operations. They still consider the work too preliminary and proprietary to release information publicly, but have assured me that effort is continuing.



Just to assure you all that progress is continuing in cost reduction for conventional melt processes, I have included some information from Dynamet Technologies on their low cost feedstock project. In this effort, they are treating scrap turnings by a proprietary method that makes them more suitable as direct feedstock for casting.

LCFP Ti-6Al-4V Casting Results

Dynamet Technology, Inc.

✓ **Chemical analyses** met applicable specs and were comparable to the baseline Ti-6Al-4V (no tramp elements).

	Al	V	Fe	C	O	N	H	Si
AMS4985/ASTMB367	5.50-6.75	3.5-4.5	0.4 max	0.1 max	0.25 max	0.05 max	0.01 max	0.1 max
Avg LCFP Casting	6.55	4.11	0.21	0.044	0.25	0.014	0.0008	0.049

✓ **Tensile Properties** met applicable specs and were comparable to wrought Ti-6Al-4V.

Material	UTS (ksi)	YS (ksi)	El (%)
Avg LCFP	155.3	137.1	12.1
AMS 4985 & ASTM B367 (castings) Min.	130	120	6.0
AMS 4928 (wrought) Min.	130	120	10.0

✓ **Projected Cost Savings: 30-60%**

August 2005

Dynamet Technology, Inc.
Eight A Street, Burlington, MA 018003

2

Results to date show chemistry and properties equivalent to ASTM standards.

Emerging Ti Extraction Technologies

Processes Producing Solid Ti

- **Issues:**
  - **Can it co-reduce alloy precursors?**
  - **Morphology?**
  - **Purity: LDI/HDI, O_2 level control, other contaminants?**
  - **Properties w/ co-reduction, BE or master alloy addition?**
  - **Cost?**
- **Candidate Processes**
  - **Armstrong / ITP**
  - **BHP Billiton**
  - **CSIR**
  - **CSIRO**
  - **FFC/Cambridge**
  - **Industrial Technologies**
  - **JTA**
  - **Kyoto Univ.**
  - **MER**
  - **MIR Chem**
  - **NIN**
  - **SATi**
  - **SRI**
  - **Univ. of Tokyo**
  - **Vartech**

Success Strategy for Advanced Materials Ventures^{SM}

Even more attention has been focused on production of solid titanium via new extraction methods. At least 15 such projects are on-going. All of these have in common the objective of by-passing melt metallurgy and on production of mill product or finished shapes via compaction of the granular or powder material. We should also mention that there is interest also in use of these materials as alternatives to Kroll sponge as melt feedstock. An increasing amount of work is now proceeding to look at the processes necessary to convert these solids to products such as sheet, plate, extrusions and finished components.

EHK TECHNOLOGIES

Armstrong / ITP

- **Technical Accomplishments**
  - **Operated commercial scale reactor successfully (200+ lb/hr production rate)**
  - **Several thousands of pounds CP Ti and alloy produced**
  - **Achieved less than 500 ppm O2**
  - **Produced homogeneous Ti-6Al-4V**
  - **Produced novel alloys**
  - **Demonstrated uniformity in microstructure**
- **Production Schedule**
  - **Currently shipping ~300 pounds per month**
  - **Modifications to current facility in progress to increase production to ~3000 pounds per month by early 2006**
  - **Pilot plant (4 million lb/yr) sited and permitting in progress; 2007 operations expected**
  - **OEM, DoD and DOE support of ITP and strategic partner production and consolidation efforts**

Success Strategy for Advanced Materials Ventures[SM]

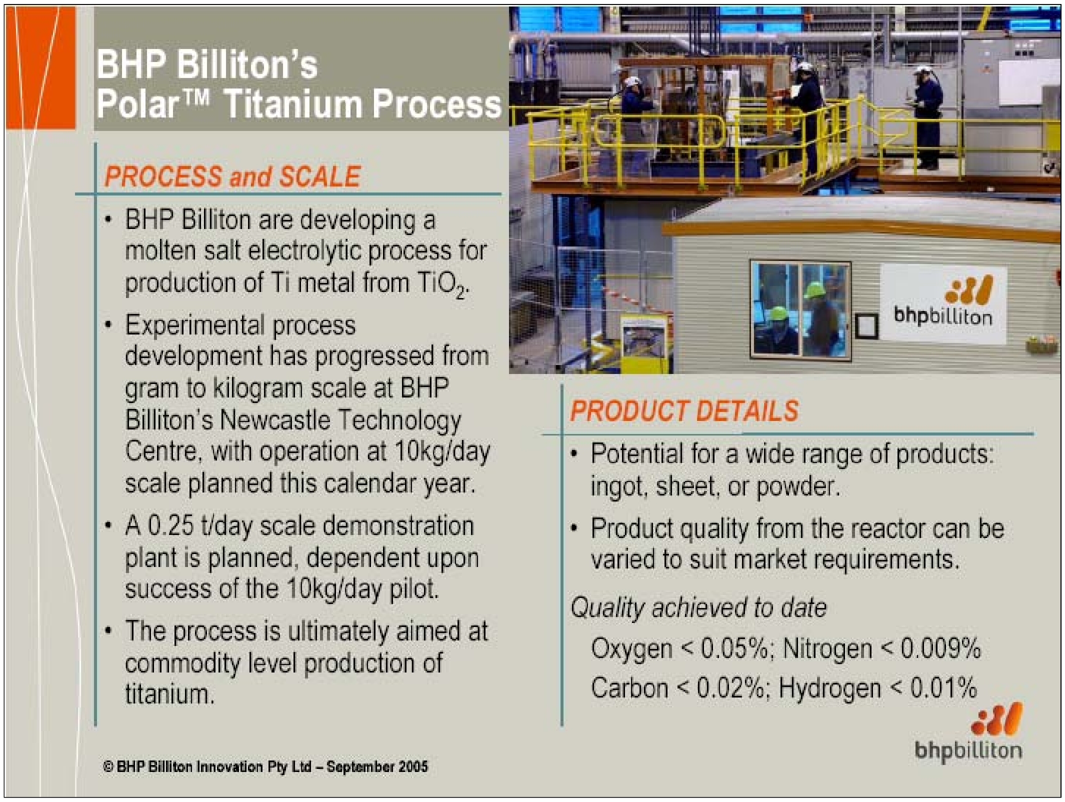
The Armstrong Process, being developed by International Titanium Powder is well along the path to commercialization. As you may recall, this process involves the reduction of $TiCl_4$ by sodium in a continuous reactor. Their commercial scale reactor has been used to produce several thousand pounds of CP and alloy titanium. Chemistry and properties of powder and consolidated shapes are very encouraging. Production at the current facility is expected to reach 3000 pounds per month early next year, and a pilot plant to produce 4 million pounds per year is expected to be operational in 2007.

Armstrong / ITP (Cont'd)

- **Consolidation Efforts with Partners**
  - Vacuum melt
  - Non-melt billet
  - Direct roll foil and sheet
  - Direct powder-to-plate for armor
  - Encapsulated advanced armor
  - Cold spray coatings
  - Press and sinter components
  - Hot press to near-net-shape
  - MIM
  - Castings
- **Commercialization**
  - Race car brake rotors produced with ITP powder currently in use
  - ITP working with OEMs to certify powder to industry specifications
  - Consolidated product from ITP powder beginning certification process

Success Strategy for Advanced Materials Ventures[SM]

ITP has been working with numerous partners in various methods of consolidation with very encouraging results. Production applications are expected in the near future in areas such as brakes, armor and other industrial, commercial and military markets. As noted, brake disks made from ITP powder are now in use on race cars. Powder and consolidated product are in the process of certification so that we can expect additional commercial applications in the reasonable future.



BHP Billiton of Australia is the World's largest diversified mineral resources company. They have been aggressively pursuing an electrolytic process over the past several years, which is beginning to show excellent results. The current 10kg/day pre-pilot scale experimental reactor has been used to characterize the process and equipment, and has achieved target quality. Further scale up is planned with the ultimate goal of flexible commodity production. A paper later in this session will be the first extensive presentation of this project.

CSIRO - Australia

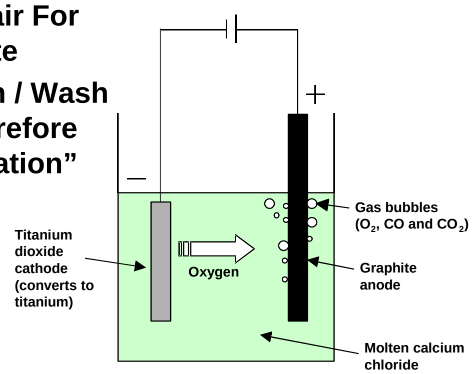
- TIRO™ Process: Continuous Reduction of $TiCl_4$ With Mg in Fluidized Bed
- Flexible Product Particle Morphology: Smooth Rounded or Whisker Covered Surface
- Present "Proof of Concept" Scale: 200g/hr; "Proof of System" Being Designed for 2kg/hr.
- Achieved: Basic Concept Demo; Quantified Efficiency & Mass Balance; Process Operating Window
- Plan: Engineering, Powder Consolidation & Partnering

Success Strategy for Advanced Materials Ventures℠

CSIRO in Australia has developed what they call the TiRO process, which is a continuous reduction of $TiCl_4$ by magnesium in a fluidized bed. One very interesting aspect of the process is it's flexibility in product morphology, from a smooth faceted particle to one coated in whiskers. They have demonstrated the basic concept in a 200g/hr rig, and are designing a "Proof of System" facility to produce 2kg/hr. Further plans include additional engineering and consolidation work and they are open to partnering discussions.

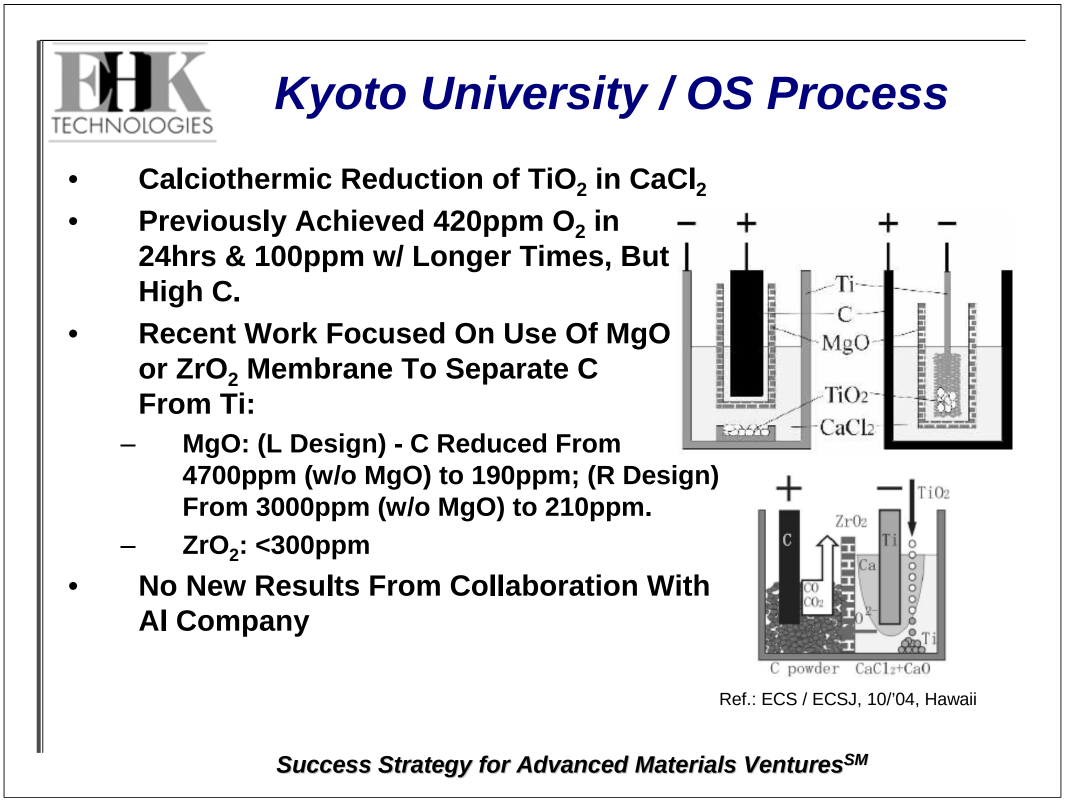
FFC / Cambridge / BTi / Timet

- Electrolytic Reduction of TiO_2 in Molten $CaCl_2$
- Original Development @ Cambridge U.; Owned and Promoted by British Titanium; Further Development and Scale Up Under DARPA Funding @ Timet
- Timet Currently in “Shakedown” of 50lb Scaleup Cell
- Timet Collaboration With Altair For High Purity TiO_2 From Ilmenite
- “As With Sponge, Acid Leach / Wash For Cl Removal Difficult, Therefore Likely To Use Vacuum Distillation”
- A Focus @ Timet on Alloy w/ Nb, V, Mo
- Recent BTi Venture Norsk Ti; Development Contract w/ Norsk Hydro

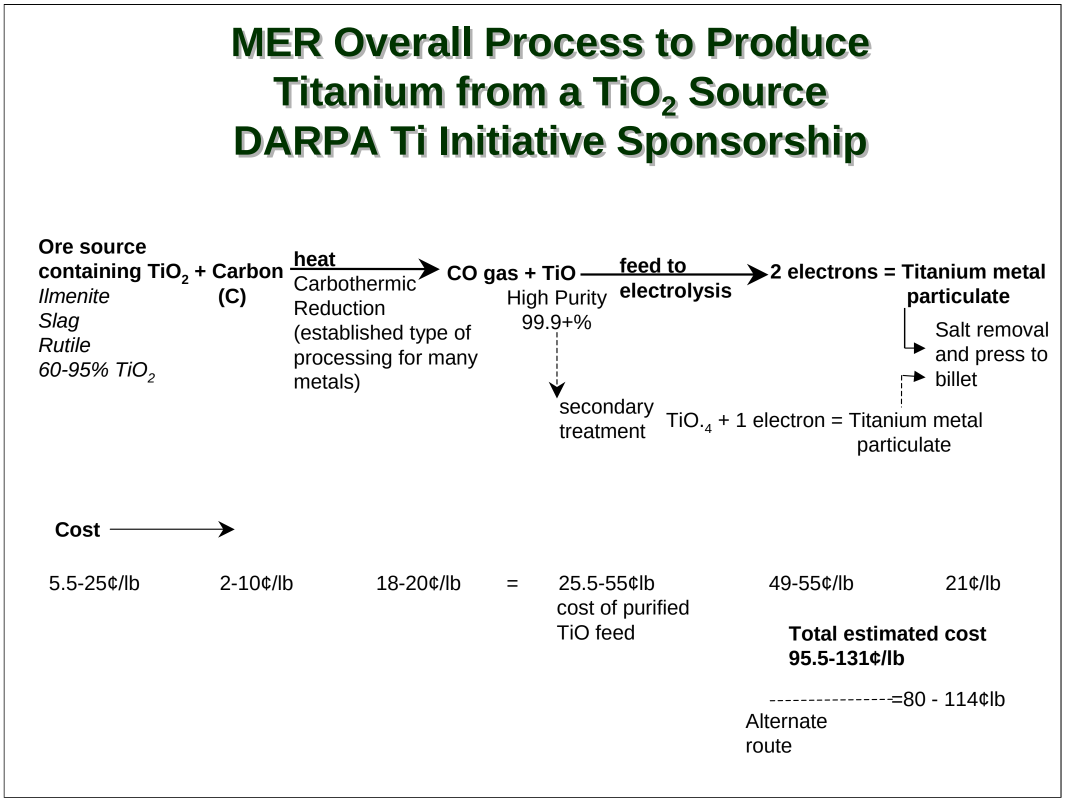


Success Strategy for Advanced Materials Ventures[SM]

Announcement of the FFC/Cambridge process a number of years ago was responsible for setting off much of the current furious pace of extraction projects. The scale up effort at Timet is continuing with current activity focused on shake down of a 50 pound cell. Timet has recognized the critical need for low cost TiO_2 feedstock and is collaborating with Altair to that end. It was recently concluded that, as with some other processes, vacuum distillation will be required to achieve required chloride levels. Also recently, British Titanium has announced formation of Norsk Titanium which will conduct additional development of the process at Norsk Hydro.



Professor Suzuki is continuing work on the process he developed with Professor Ono, who is now retired. This is a calciothermic process to reduce TiO_2 in $CaCl_2$. Earlier difficulty with carbon contamination is now being addressed by use of MgO or ZrO_2 membranes, which have both been shown to be effective. Lab work is continuing, but he reports that the earlier announced collaboration with a large aluminum company has not produced any new results.

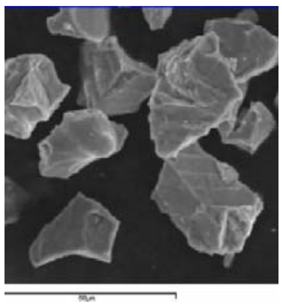


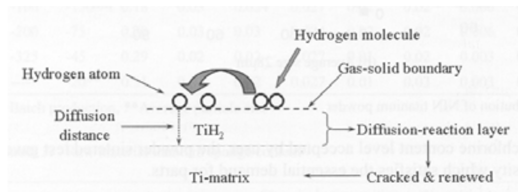
MER in nearby Tucson has continued their work under the DARPA Ti Initiative. Their system provides several paths to Ti, all of which involve both partial reduction with carbon followed by electrolytic reduction. The use of carbon is proposed to lower overall cost. Careful control of stoichiometry has been identified as a key factor in achieving product quality. Very low cost is expected by the developers.

NIN

Northwest Institute for Nonferrous Metal Research (China)

- **“Motive Hydrogenate/Dehydrogenate” (MHDH) Process**
- **Combines and Reduces Number of Process Steps From 6 to 2**
- **Promotes Breaking of Hydride Layer to Double Rate**
- **Sponge Feedstock Cl Reduced From 0.06/0.08% to 0.02/0.03%**
- **Feedstock: Sponge, Scrap; CP or Alloy**
- **Projected cost $7.9 – 9.5 / kg**

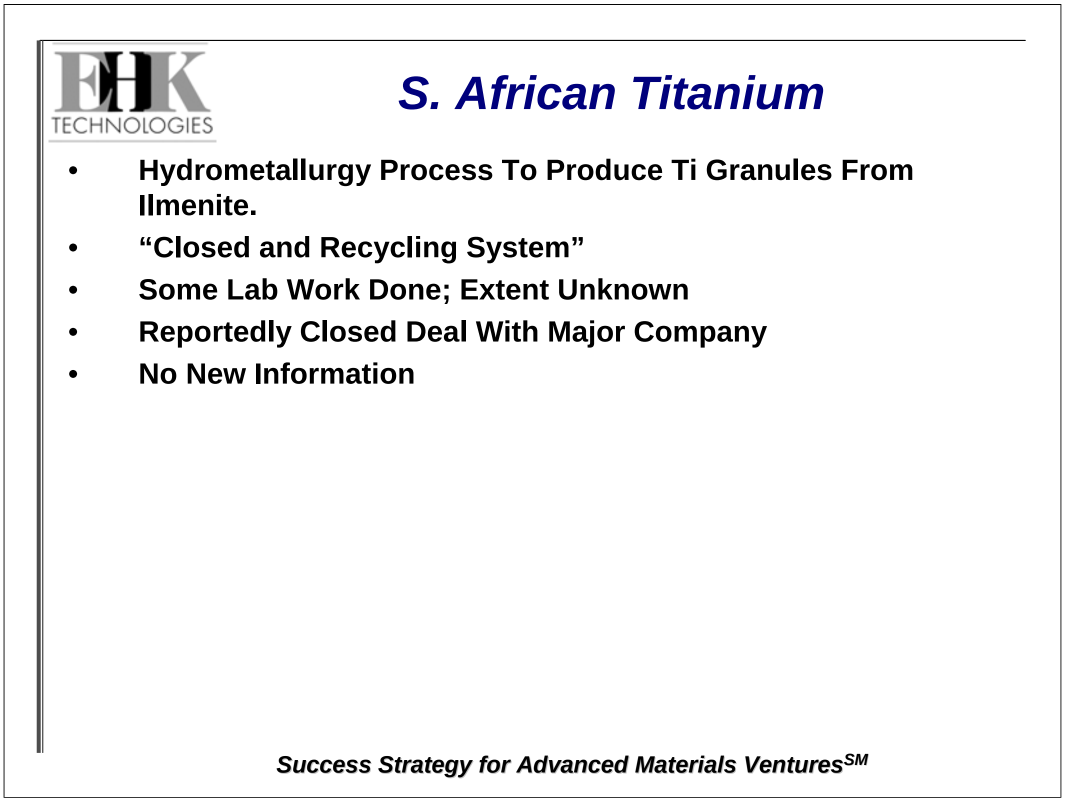




(Ref. Ti 2003;Hamburg; pp. 482-3)

Success Strategy for Advanced Materials Ventures[SM]

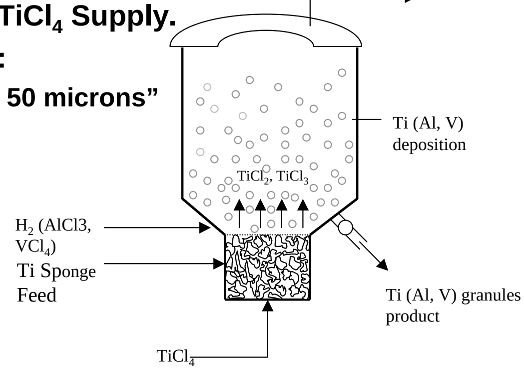
While not actually an extraction process, the “Motive Hydrogenation/Dehydrogenation” or MHDH process being developed at NIN in Xian, China is of interest due to projected low cost. By integrating processes and adding a step to continuously provide fresh surface, NIN has reduced steps from 6 to 2 or 3 and doubled the production rate. Significant reduction in chloride from the sponge feedstock has been achieved and projected cost of $7.5 to $9.5 / kg is attractive.



A paper on a process by S. African Ti was on the program at Monterey two years ago but withdrawn at the last moment. My subsequent discussions with this group revealed that the reason was intense discussions with a partner company. More recent information is that some arrangement with a major company has been concluded. Little detail was revealed other than that it is a hydrometallurgical process producing granules from Ilmenite.

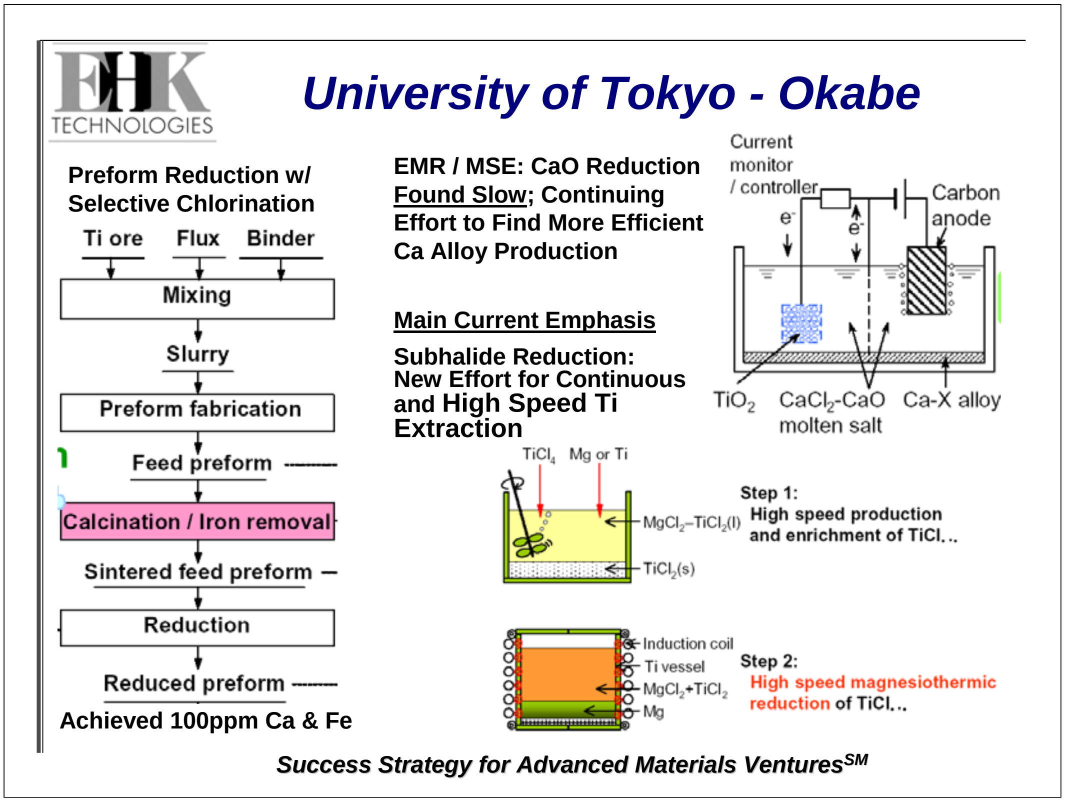
SRI

- H_2 Reduction of $TiCl_4$ in Fluidized Bed
- Deposition of Ti or Alloy on Particulate Substrate (Sponge fines or fine particle size product fraction)
- Recent Focus on Improved Thermochemical Model
- Millennium / Lyondell No Longer Involved; Will Focus On Core Business, Including $TiCl_4$ Supply.
- Deposition Rates in Trials:
  - "Hours Run Time for 30 – 50 microns"
  - 1micron in 40 minutes



Success Strategy for Advanced Materials Ventures[SM]

Work is continuing at SRI on improving the fundamentals of their fluidized bed process for reduction of $TiCl_4$ by hydrogen. Deposition rates in this process appear to be rather slow, but perhaps the recently improved thermochemical modeling will provide an improved operating widow. The previous involvement of Millennium Chemical, now part of Lyondell, is no longer in effect. We should be clear that the reason for this does not involve the SRI process itself, but is a result of a decision by Lyondell to focus on core businesses including $TiCl_4$ supply.



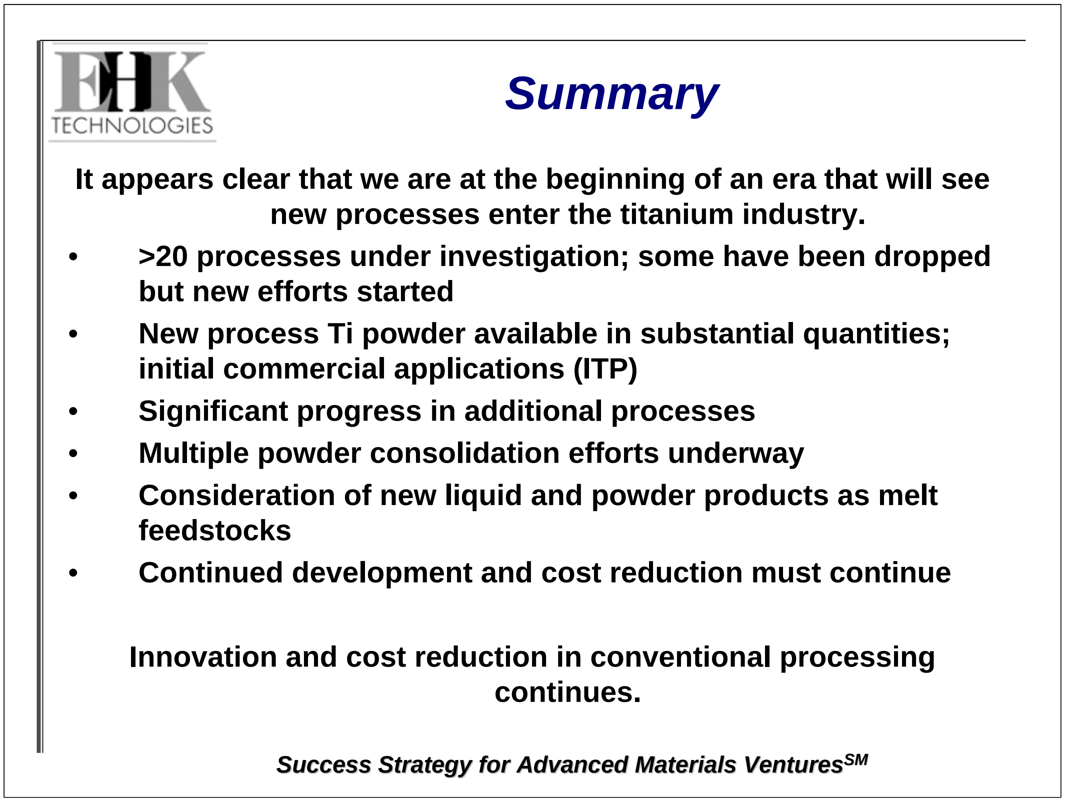
Professor Okabe has been extremely busy with several processes and variants for $TiCl_4$ reduction. One interesting variant on the preform reduction process is addition of a selective chlorination step which allows use of low cost ore as feedstock. He has asked me to mention that his main focus is currently on what he calls "Continuous and High Speed Reduction," which involves successive reduction of subhalides.

Idaho Ti Technologies / Vartech

- Hydrogen Plasma Reduction of $TiCl_4$
- ~'96 – '99, Navy Contract to ITT to Develop Reactor
- Achieved 15kg/hr.
- NIST Contract ~'01 – '04 for Particle Size Increase; Achieved ~10X Increase Via Recirculating Classified Fine Fraction Through Condensation Zone.
- Vartech Effort For TiAl; Seeking Additional Funding For Ti

Success Strategy for Advanced Materials Ventures[SM]

Vartech and the Idaho Titanium Technologies group have been seeking to develop the hydrogen plasma reduction of $TiCl_4$ for almost 10 years. Early efforts succeeded in producing 15kg / hour of titanium. The process was plagued by the very fine, submicron, particle size produced which made handling very difficult. Some progress was achieved in increasing this size. Another contract investigated application to TiAl. Current activities are minimal pending further funding.



In summary, we can see that we are at the beginning of an era that will see new processes for lower cost enter the titanium industry. Over 20 processes are under investigation around the world. Some processes have been dropped, but new efforts have been started. We now have available Ti powder from one new process, that at ITP, being produced in substantial quantities and being used in initial commercial application. Significant progress is being reported in additional processes. The efforts to develop consolidation methods for these powders has accelerated. New powders and liquid Ti products are being considered as melt feedstocks to supplement or replace traditional materials. With these promising developments, it is clear that development must continue along with additional cost reduction steps. Lastly, we are also fortunate that innovation and cost reduction is continuing in conventional processing, so that even when or if the current boom cycle in existing markets comes to an end, new technologies will allow the industry to enter a new era of expansion.

Thank you for your attention. I would be happy to try to answer your questions on these activities, or to discuss the subject during the breaks.