Powder Metallurgy of Titanium

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Motivation for Powder Metallurgy Approach to Produce Titanium and Titanium Alloy Components

Titanium alloys are attractive materials for many structural applications due to:

- high strength

- low density

- good corrosion resistance

BUT: high cost restricts their application

The main trend in titanium material science is to expand application of titanium alloys by development of new technologies that provide significant cost reduction

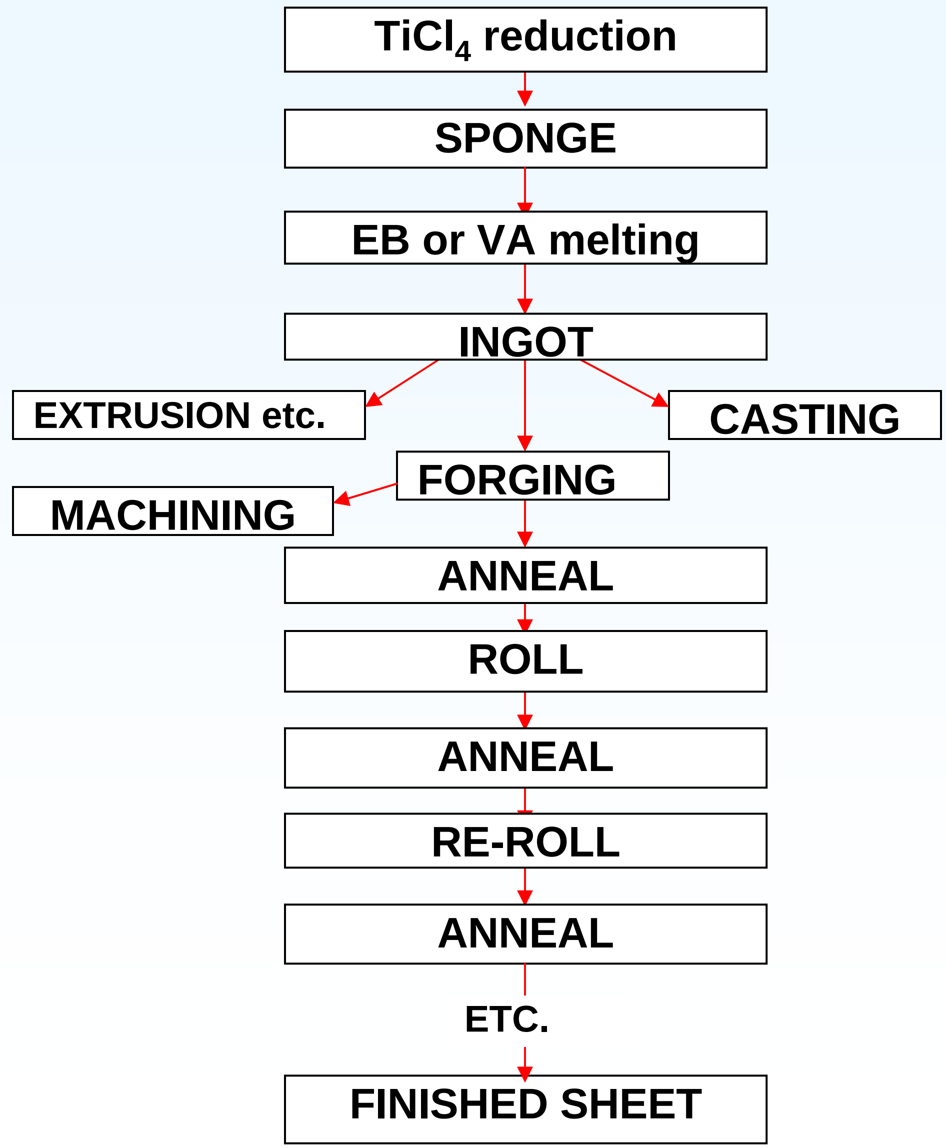
Why Does Titanium Presently Cost So Much?

High extracting costs

- strong bonding between titanium and oxygen;
- requirements to get relatively low levels of other elements;

High processing costs

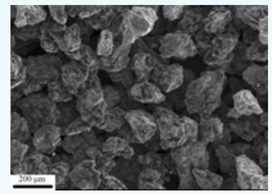
- high temperature processing requires conditioning prior to further fabrication (surface regions contaminated at the processing temperatures, and surface cracks, both of which must be removed);



Achieving Much Lower Cost

• Reducing High Extracting Costs

Innovative Ti powder production technologies



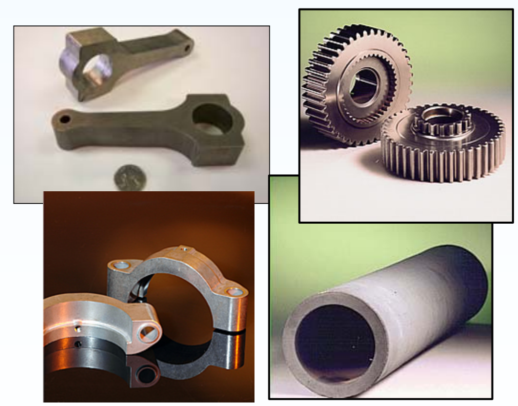
• Reducing High Processing Cost

Blended Elemental Powder Metallurgy Approach

Cost-Effective Ti Powder →

Simple Consolidation →

Sinter →



Finished Products with Good Mechanical Properties

Titanium Powder Production

HDH Process

Titanium Powder Production

ADMA Process

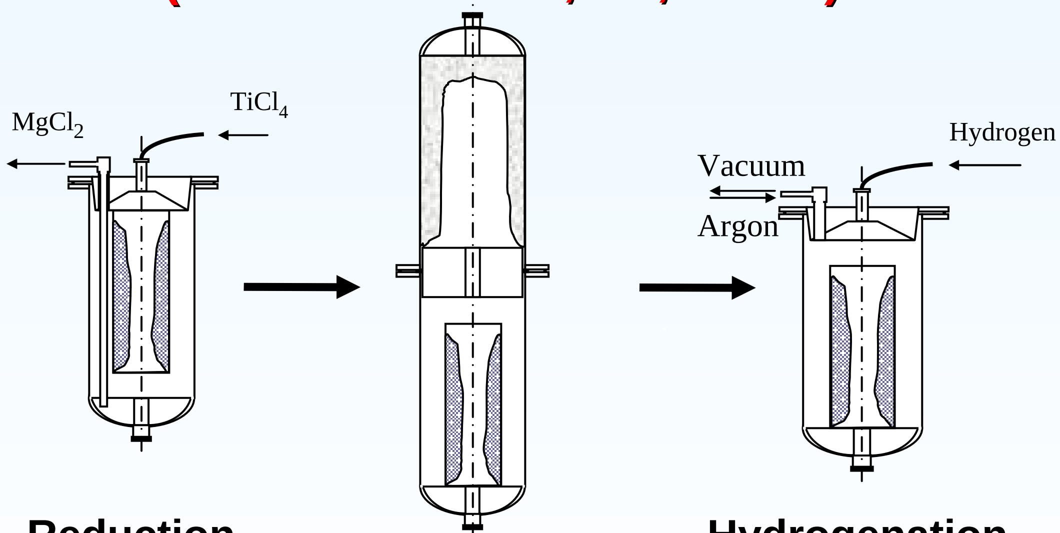
(U.S. Patent No. 6,638,336 B1)

~~Ti sponge block~~

~~(Kroll process)~~

Hydrogenated Ti sponge block

(Modified Kroll process)



Reduction

Vacuum distillation

Hydrogenation

Hydrogenated powder

Hydrogenated Ti sponge block crushing

ADMA Process vs Kroll Process

Hydrogenated Ti sponge block

(Modified Kroll process)

vs

Ti sponge block

(Kroll process)

Cost reduction

- easier crushing
- underseparated
- shorter time
- lower energy
- lower labor

≈

Cost increasing

- hydrogenation

Cost of Hydrogenated Powder ≈ Cost of Titanium Sponge

High-Dense (98-99%) Blended Elemental P/M Titanium Alloy Parts

TiH$_2$
~~Ti~~, Alloying Elements Powders

↓ Blending

Powder Blend

↓ Compaction

BE Compact (NNS)

↓ Sintering

Component

↓

~~HIP~~

↓

Low Porous Component

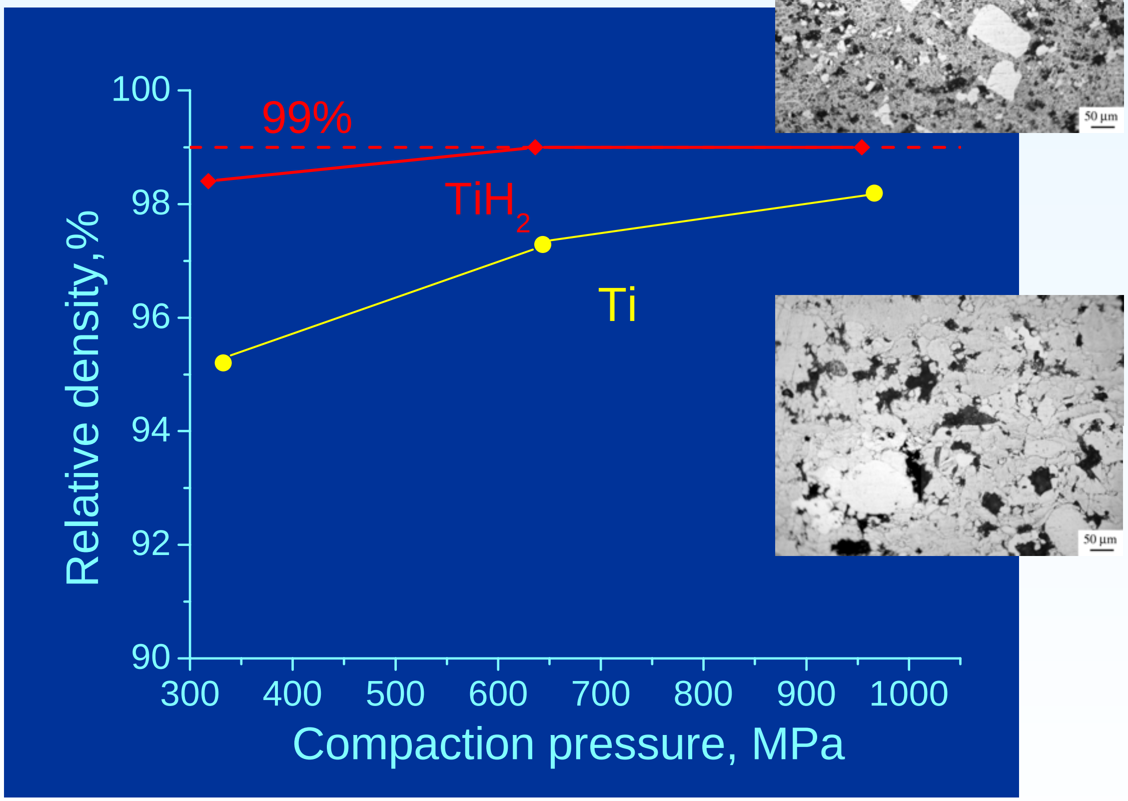
Blends based on Ti powder: post-sintering working operations (HIP or hot deformation) are necessary → Increase in cost

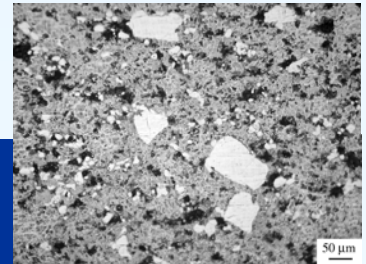
Employment of TiH$_2$ instead of Ti powder allows attainment of 99% density and mechanical properties equivalent to those of ingot materials with most cost-effective press-and-sinter approach (without HIP)

- **Specific mechanism of compaction → optimized green porosity**
- **Shear type phase transformation TiH$_2$→Ti (β or α) → high density of crystal lattice defects**
- **Surface self reducing by atomic hydrogen**

→ Faster sintering, higher sintered density, lower impurity content

Influence of Compaction Pressure





TiH_2 – based compacts:
-Fine crushed hydride fragments;
-Fine pores independently on pressure applied
Pores are easy to heal upon sintering
→ high sintered density

Ti – based compacts:
-Deformed ductile particles;
-Relatively coarse pores (size depends on pressure applied);
Pores partially survived upon sintering

Density: To attain sufficient sintered density compaction pressure value is not critical parameter for titanium hydride powder contrary to titanium powder.

This unique feature of the titanium hydride approach is attributed to compaction mechanism of low strength and brittle hydride particles.

Residual Hydrogen

Hydrogen content is reduced to safe level 20-60 ppm even at production of components with large cross-sections

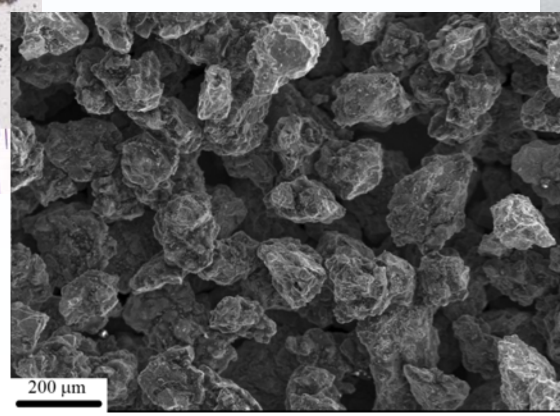
Ti-6Al-4V billet 8.50” x 12.0” x 52.0”
725 lbs

Sample Identification:	Ti-Grade 5
	%
Aluminum	6.26
Vanadium	4.4
Oxygen	.179
Iron	.077
Hydrogen	.0018
Carbon	.010
Nitrogen	.016
Manganese	.011
Total Others	<.4
Titanium	Balance

Chemistry of Commercially Available Hydrogenated Titanium Powder

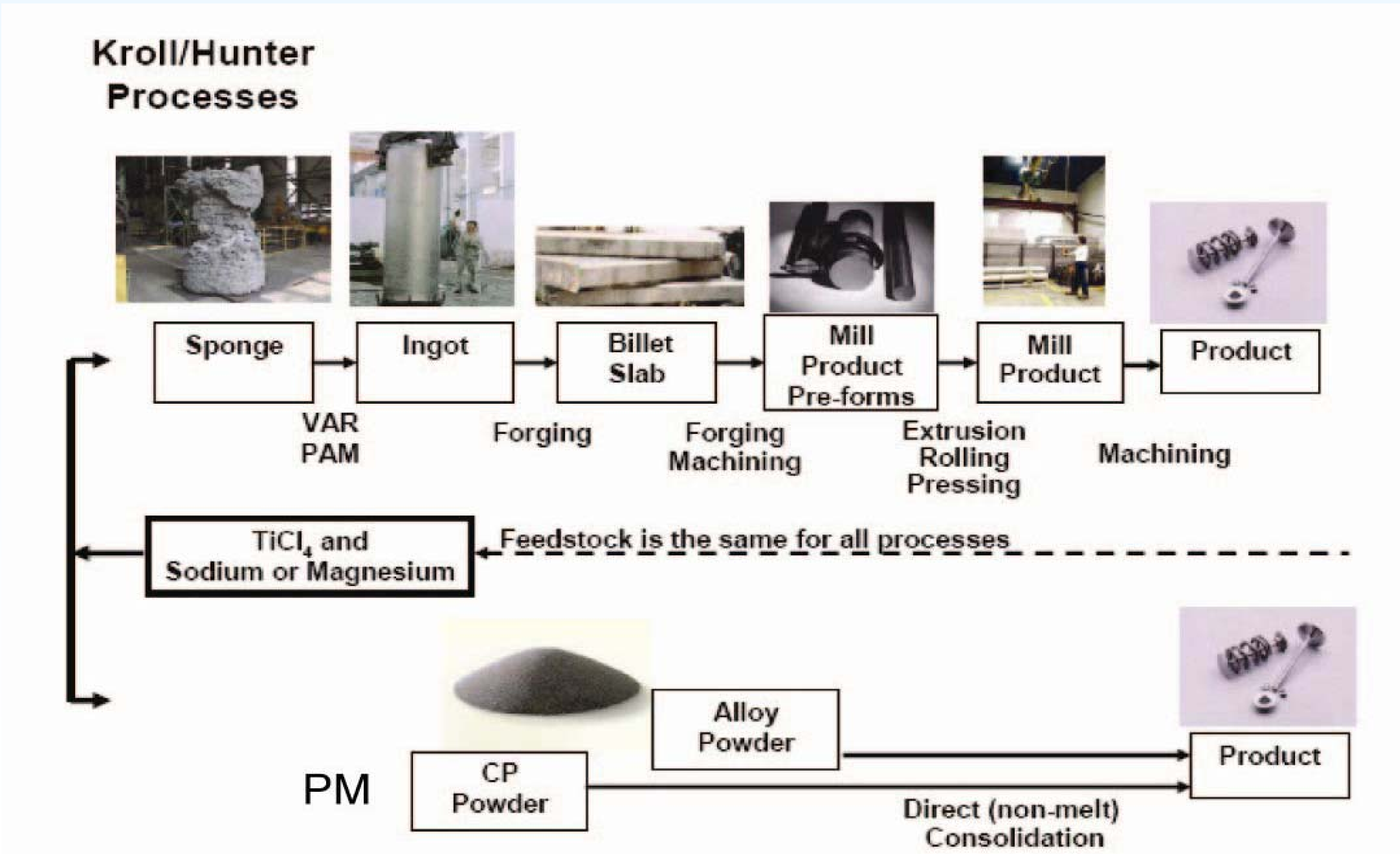
	Cl	Fe	Ni	C	N	O	H
Hydrogenated Sponge	0.05	0.062	0.052	0.008	0.013	0.06-0.08	3.85
Powder -150 μm	0.054	0.054-0.073	0.041	0.005-0.008	0.011-0.013	0.09-0.10	3.90

TiH_2 sponge



TiH_2 powder (-100 mesh) grinded at ADMA Products, Inc.

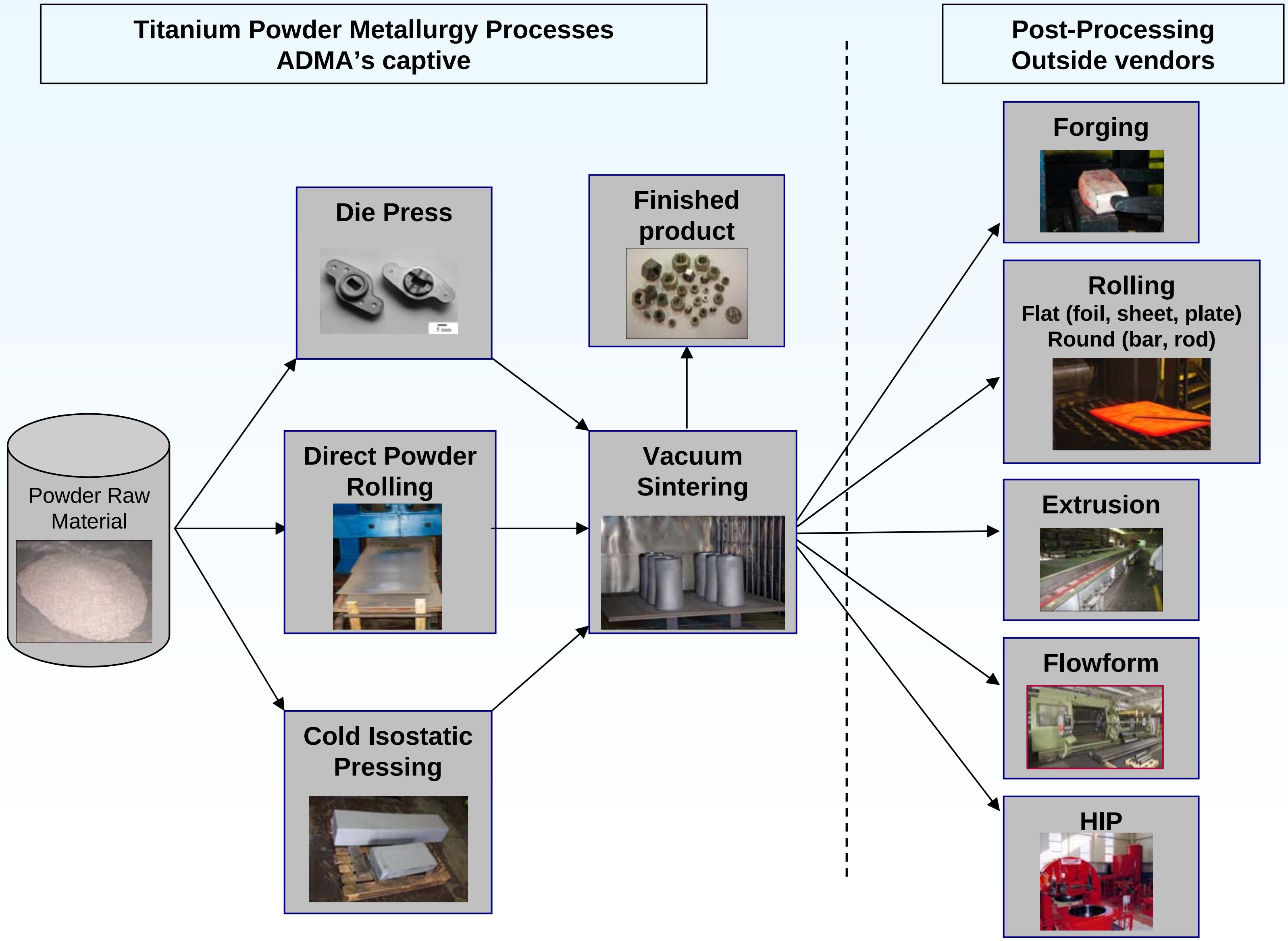
Powder metallurgy, especially blended elemental powder metallurgy (BEPM) approach at which alloying elements are added to titanium powder as elemental or master alloy powders enables significant reduction in the cost



Benefits of P/M Processing

- **Fewer steps**
- **No extensive secondary machining**
- **Low buy-to-use ratio: scrap rate ≤ 2%**
- **Direct alloying**
- **Rapid manufacturing cycle**
- **Uniform properties in longitudinal and transverse directions**
- **No texture developed**
- **Integral processing of composites, laminates or functionally gradient plate**
- **More energy efficient**

Processing Steps for the B/E Ti Alloy Parts Production



Low-Cost Room Temperature Consolidation

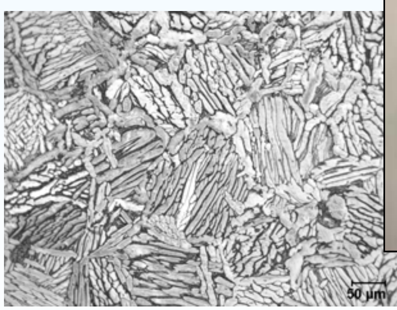
Die-Press + Sinter

P/M Titanium Alloy Components

Die Pressing + Sintering

Near Net Shape

Die Pressing → Sintering



Material	Composition, %							
	N	C	H	Fe	O	Al	V	Ti
P/M Ti-6Al-4V	0.019	0.014	0.0014	0.05	0.13-0.26	6.32	4.23	Bal
ASTM B 817-98, Type I	0.04	0.10	0.015	0.40 max	0.30	5.50 – 6.75	3.50 – 4.50	Bal

Low-Cost Room Temperature Consolidation

Direct Powder Rolling + Sinter

Production of Solid State Titanium Plate: Direct Powder Rolling

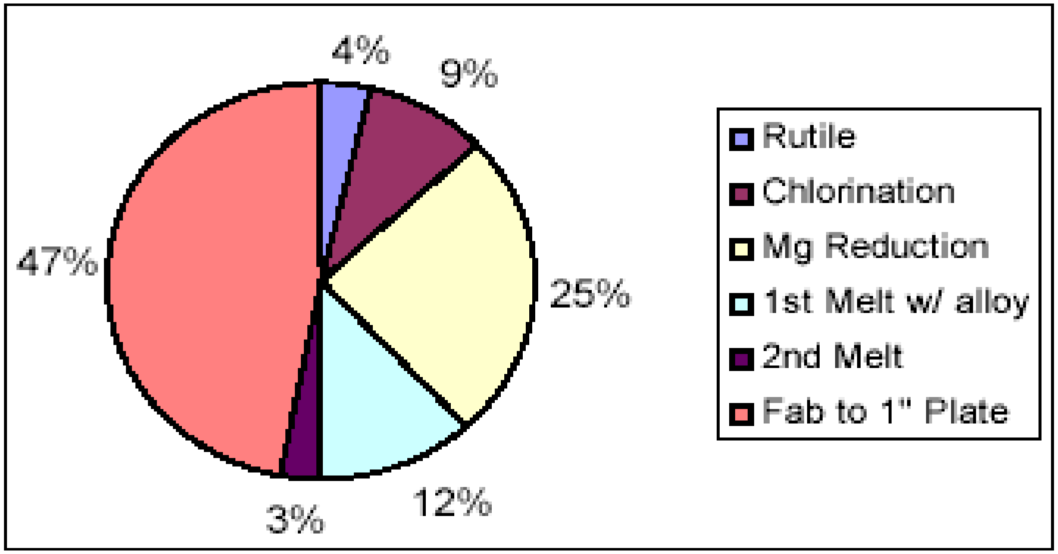
Relative Cost Factors for Conventional and PM Processing of 1" Ti Alloy Plate

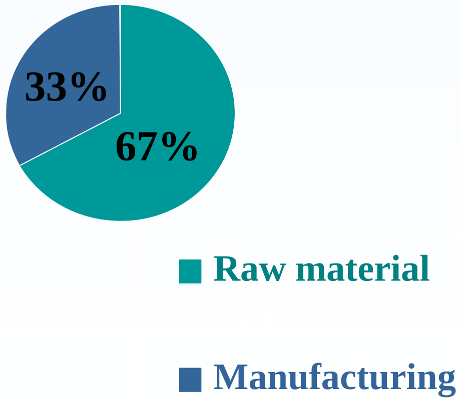
Wrought Ti Alloy Plate

Delivery: - 50-80 weeks

PM Ti Alloy Plate

Delivery: - 4 weeks





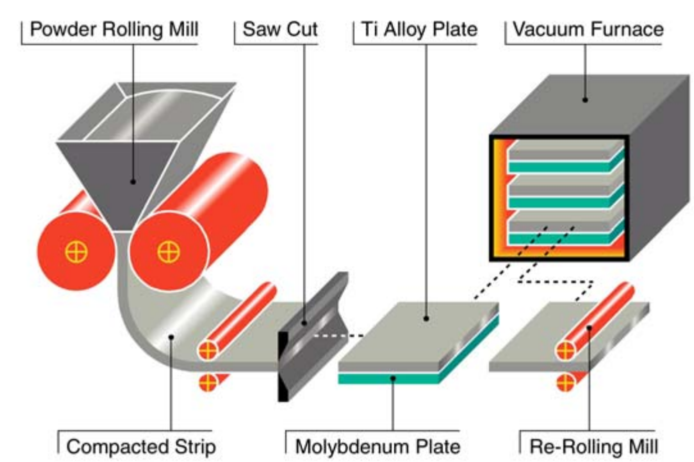
Comparison of the conventional sheet process with the direct powder rolling process for Ti-6Al-4V alloy

Conventional

INGOT
↓
FORGING
↓
ANNEAL
↓
ROLL
↓
ANNEAL
↓
RE-ROLL
↓
ANNEAL
↓
ETC.
↓
ETC.
↓
FINISHED SHEET

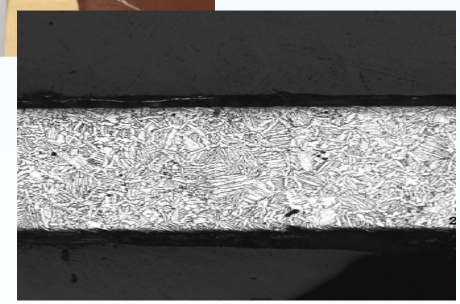
Direct Powder Rolling

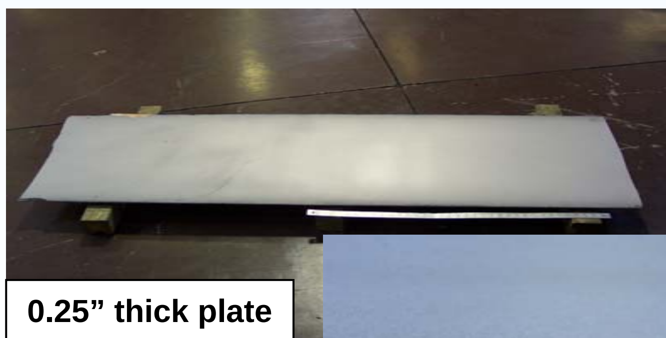
Elemental Ti Powder → BLEND ← Alloying Powders
↓
POWDER ROLLING
↓
SINTER
↓
RE-ROLL
↓
ANNEAL
↓
FINISHED SHEET



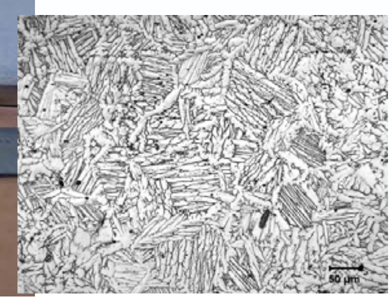
Direct Powder Rolling of Ti Alloy Foil, Sheet, and Plate at ADMA

0.010” thick Ti foil

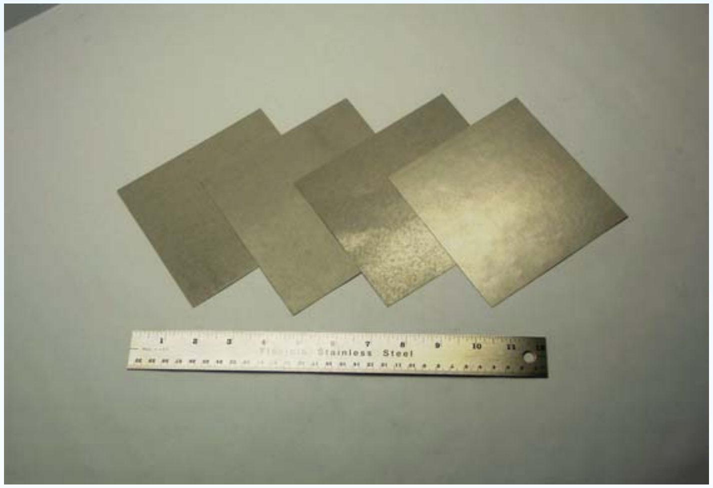


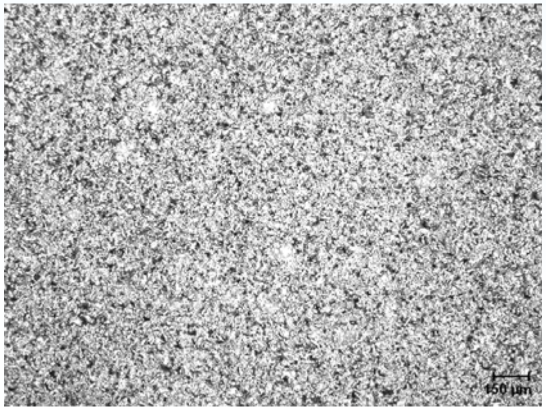


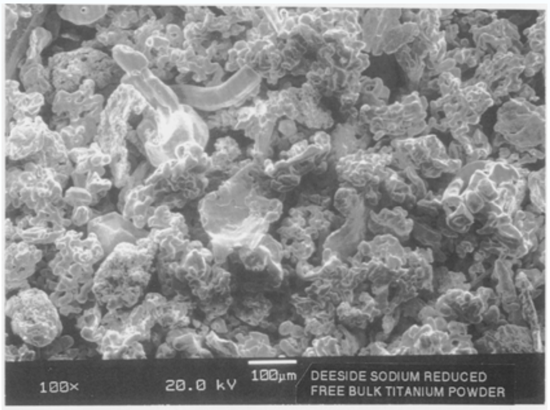
0.25” thick plate



Porous Titanium, Zirconium, Niobium, and Stainless Steel Plates







Life support systems for various applications

Low-Cost Room Temperature Consolidation

Cold Isostatic Pressing + Sinter

Titanium or Titanium Alloy

Cold Isostatic Pressing + Sintering

Cold Isostatic Pressing

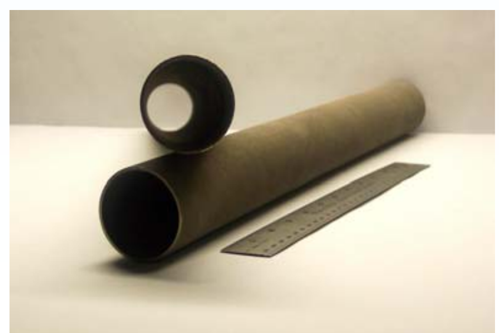
↓

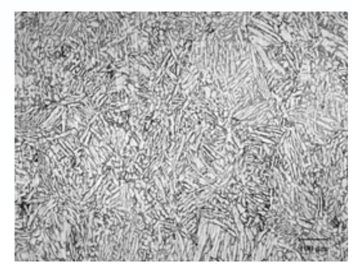
Sintering

↓

Post-processing

- Forging
- Flowform
- Rolling
  - Flat (foil, sheet, plate)
  - Round (bar, rod)
- HIP
- Extrusion





P/M Ti-6Al-4V billets produced by low cost CIP/Sinter/Forging approach

Cold Isostatic Pressing

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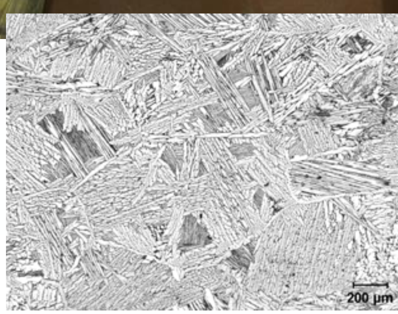
Sintering

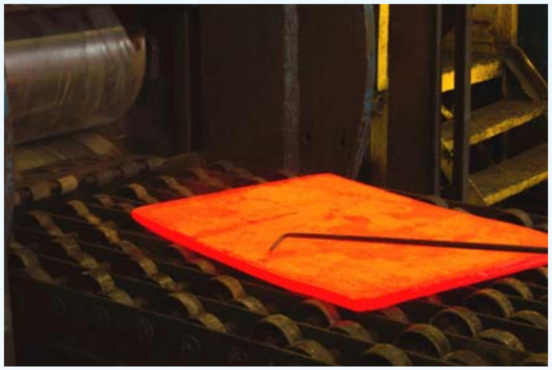
↓

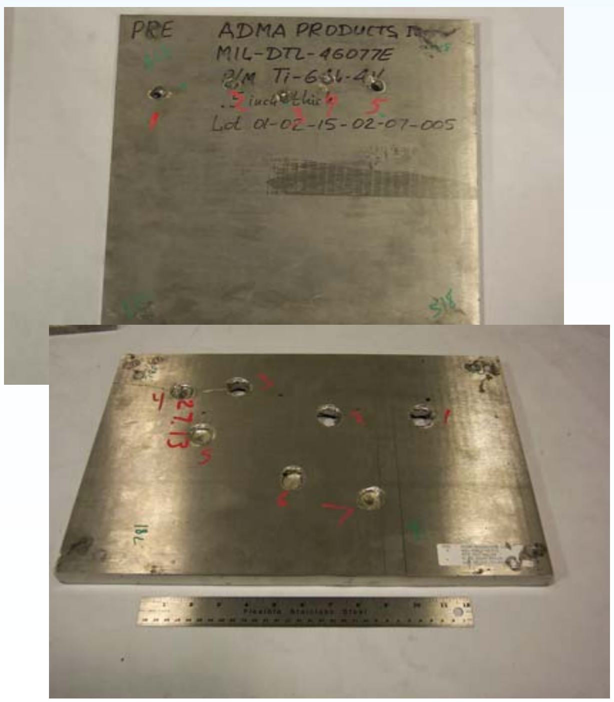
Forging



P/M Ti-6Al-4V Armor Plates from Hydrogenated Ti powder

0.75" thick





Cold Isostatic Pressing

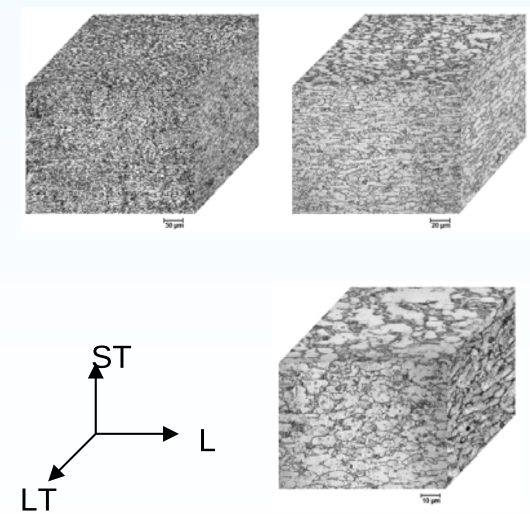
↓

Sintering

↓

Rolling

0.50" thick



L – Longitudinal
LT – Long transverse
ST – Short transverse

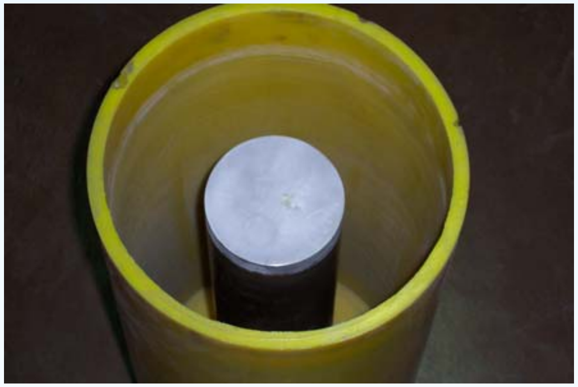
P/M Ti-6Al-4V Armor Plate from Hydrogenated Ti powder

Elements, %										
Al	V	C	Cl	Fe	H	N	Na	O	Si	Ti
6.04	4.28	0.010	<0.001	0.070	0.0017	0.030	<0.005	0.295	0.01	Bal.

ASTM E8 ROOM TEMPERATURE TENSILE TEST

	P/M Ti-6Al-4V		MIL-DTL-46077F	ASTM B265
	Sample 1	Sample 2		
UTS (PSI)	154,000	154,500	120,000	130,000
0.2% YS (PSI)	138,000	138,000	110,000	120,000
ELONGATION, %	15	15	10	10
R. A., %	34	36	-	25

P/M Ti and Ti alloy Hollow Pre-forms for Tubes and Pipes



CIP → Vacuum Sintering → Flowform

ADMA Hydrogenated Ti Powder

Ti Grade 2 –ADMA's Preforms Flowformed into 4" schedule 10 Pipe - 86% wall reduction during flowforming

- Titanium pipe system **saves 178,000 lbs.** per LPD compared to Cu-Ni pipe system Ship improving fuel efficiency and reducing life cycle maintenance cost of the pipe system
- It is estimated that a titanium piping system could **save $17M** per ship (LPD) considering life cycle savings, NAVSEA Carderock[1]

Flowformed titanium pipe Preforms

Material	Ultimate Strength, psi	Yield Strength, psi	Elongation, %
ADMA P/M Grade 2	110,000	94,000	16

Courtesy Dynamic Flowform Inc.

Blended Elemental P/M Ti-6Al-4V Billets for Extrusion

CIP

↓

Vacuum Sintering

↓

Extrusion

Canless Extrusion Process Development for Blended-Elemental Powder-Based Titanium Ti-6AL-4V Alloy

The Boeing Company (Phantom Works)
ADMA Products, Inc.
Plymouth Engineered Shapes, Inc.
RTI International Metals, Inc.

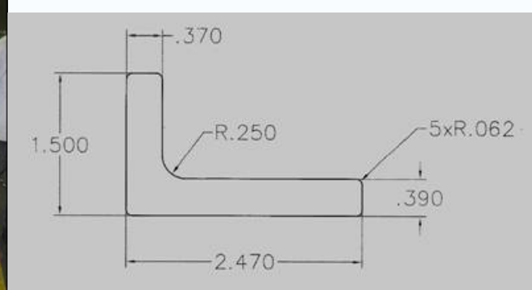
Canless Extrusion Process Development for Blended-Elemental Powder-Based Titanium Ti-6AL-4V Alloy (Boeing/ADMA)

ADMA-fabricated Ti-6AL-4V blended elemental powder-based billets were extruded successfully by Plymouth Engineered Shapes, Inc. and RTI International Metals, Inc.

Plymouth Engineered Shapes, Inc.

Extrusions up to 27-foot long were fabricated and analyzed at front, mid-length, and back and found to be uniform with respect to oxygen content & microstructure. Longer and larger cross-section fabrication is a non-issue in this process.

RTI, International Metals, Inc.



36'-Long Extrusions Cut-up for Shipping and Laboratory Characterization

Ti-6Al-4V	Ultimate Strength, (ksi)	Yield Strength, (ksi)	Elongation, %	Elastic Modulus, MSi
ADMA P/M	136.5	149.6	15.8	16.9
Ingot Based	129.0	141.5	14..5	17.4

Boeing–Obtained Results of Chemical Analyses of Extruded Parts Showed Blended Elemental Powder-Based Parts Conforming to Ti-6Al-4V Except for Oxygen Content

Table - Results of chemical analyses* of blended-elemental powder-based titanium Ti-6AL-4V extrusions per 787 Part DWG # BAC 1670-157 extruded by RTI International Metals, Inc. per AMS 4934G and 4935G.

Material Product Form	Extrusion Process Tempera-ture/ Regime	Sample Position Within Extrusion Along 8' length	Sample Identifi-cation	Chemical Element Weight Percent										
				AL [%]	V [%]	Fe [%]	O [%]	N [%]	H ppm	C [%]	Y [%]	OEE [%]	OET [%]	Bal. [%]
Ti Billet CIP/Sintered	As-Sintered	Billet End OD Sample	Billet # 5	6.13	4.33	0.15	0.37	0.01	69	0.01	<0.005	<0.10	<0.40	Ti
Extrusions	R1 Extrusion Beta-Extruded At High Temperature	Front	R1F2	6.36	4.15	0.14	0.35	0.02	249	0.01	<0.005	<0.10	<0.40	Ti
		Middle	R1M2	6.32	4.13	0.14	0.35	0.02	394	0.01	<0.005	<0.10	<0.40	Ti
		Back (Rear End)	R1B4	6.30	4.03	0.19	0.33	0.02	379	0.01	<0.005	<0.10	<0.40	Ti
	R2 Extrusion Beta-Extruded at Lower Temperature	Front	R2F2	6.55	4.01	0.15	0.29	0.02	244	0.01	<0.005	<0.10	<0.40	Ti
		Middle	R2M2	6.52	4.12	0.15	0.29	0.02	307	0.01	<0.005	<0.10	<0.40	Ti
		Back (Rear End)	R2B4	6.22	4.20	0.15	0.29	0.02	332	0.01	<0.005	<0.10	<0.40	Ti
	Ingot-Based Billet R4 Extruded at Same Temperature as R2	Front	R4F2	5.88	3.94	0.17	0.20	0.01	25	0.02	<0.005	<0.10	<0.40	Ti
		Middle	R4M2	6.10	4.02	0.18	0.20	0.01	24	0.02	<0.005	<0.10	<0.40	Ti
		Back (Rear End)	R4B4	6.22	3.96	0.18	0.20	0.01	34	0.02	<0.005	<0.10	<0.40	Ti
Ti-6AL-4V AMS 4934	Extrusion	All	Min. Max.	5.50 6.75	3.50 4.50	0.30	0.20	0.05	125	0.10	0.005	0.10	0.40	Ti

*** All samples were analyzed at Durkee Testing Laboratories, Inc. Los Angeles, CA, using emission spectroscopy and inert gas fusion method. The Laboratory Purchase Order Number is 315427 to AMS 4934D and 4935G. and the Lab. Log Number 207616A.**

Boeing–Obtained Results of Tensile Properties in Extruded Parts Showed B-E Powder-Based Properties Superior to Ingot-Based Same Alloy

Table 1 – Comparison of room-temperature tensile properties of extruded product forms from Blended elemental ADMA-Consolidated hydride/dehydride powder subsequently extruded by RTI and Plymouth (with final product containing 3000 ppm oxygen) versus ingot-based extrusions (with 2000 ppm Oxygen maximum)

Part ID	Material: Powder or Ingot / Extrusion Process	Test Specimen Location within Extrusion	UTS [ksi]	0.2% σ_Y [ksi]	E% [%]	Elastic Modulus [Msi]	UTS [ksi]	0.2% σ_Y [ksi]	E% [%]	Elastic Modulus [Msi]	Notes on Extrusion Tempera-tures
P-1	B-E / Beta	Front	145.9	131.3	16	16.5	145.1	130.4	16.3	16.6	Beta Extrusion
	B-E / Beta	Mid span	144.6	130.1	16.5	16.2					
	B-E / Beta	Back	144.9	129.7	16.5	17					
P-2	B-E/@ β tr.	Front	150	136.8	16.5	16.4	150.1	137.0	15.8	17.1	Extruded at Beta Transus
	B-E/@ β tr.	Mid span	149.8	136	15.5	17.3					
	B-E/@ β tr.	Back	150.4	138.3	15.5	17.6					
P-3	B-E/ α–β	Front	150.3	137.8	16	17.1	149.4	136.9	16.0	17.0	Lowest Extrusion Temp.
	B-E/ α–β	Mid span	148.7	135.9	16	16.8					
	B-E/ α–β	Back	149.3	137	16	17.1					
R1	B-E / Beta	Front	155	142.6	14.5	17.1	151.9	139.2	15.2	16.8	Highest Extrusion Temp.
	B-E / Beta	Mid span	153.5	140.7	15.5	16.2					
	B-E / Beta	Back	147.2	134.4	15.5	17.2					
R2	B-E / Beta	Front	151.4	139.8	15	16.8	151.3	138.8	15.5	16.9	Same Temp. as for R4
	B-E / Beta	Mid span	150	137.2	16	17					
	B-E / Beta	Back	152.4	139.3	15.5	16.9					
R4	Ingot/ Beta	Front	146.8	134.9	15	17	141.5	129.0	14.5	17.4	Same Temp. as for R2
	Ingot/ Beta	Mid span	139	125.6	14.5	17.5					
	Ingot/ Beta	Back	138.6	126.4	14	17.6					
Overall Average Properties (36 Tests)						Powder	149.6	136.5	15.8	16.9	B-E 6% Stronger
						Ingot	141.5	129	14.5	17.4	

Boeing-Obtained Summary on Canless Air-Extruded Product Form

- Canless full-scale extrusion of blended elemental hydride/dehydride ADMA powder-based product form has been successfully demonstrated.
- Any residual hydrogen content within the final extruded parts was thermally degassed in vacuum down to 23-33 ppm.
- Preliminary encouraging powder-based extruded product form shows static tensile and fatigue S/N durability properties superior to ingot-based identically extruded product form.
- Further optimization should focus on reducing oxygen content in the final blended elemental powder based product down to 2000 ppm maximum for aerospace quality material.

Low-oxygen P/M Ti-6Al-4V Billets from Hydrogenated Ti Powder

Ti-6Al-4V billet 8.50” x 12.0” x 52.0”
725 lbs

Sample Identification	H09-02-25.1/01	
	%	
Oxygen	.143	
Carbon	.009	
Nitrogen	.012	
Hydrogen	.0275	.0269
Aluminum	6.01	
Vanadium	4.12	
Iron	.085	
Yttrium	.0008	
Chromium	.022	
Nickel	.024	
Silicon	.016	
Total others	<.40	
Titanium	Remainder	

Low-oxygen P/M Ti-6Al-4V CIP/Sinter Pre-forms

Cold Isostatic Pressing

Sintering

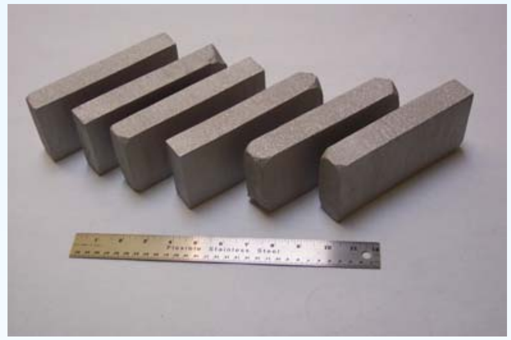
Forging

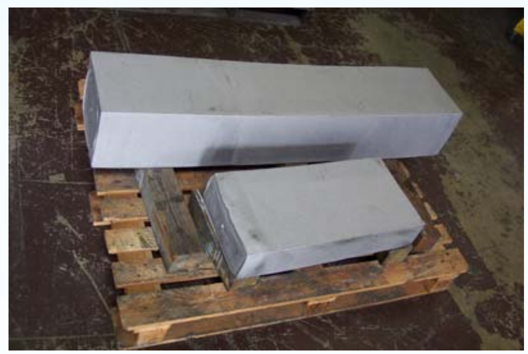
Rolling

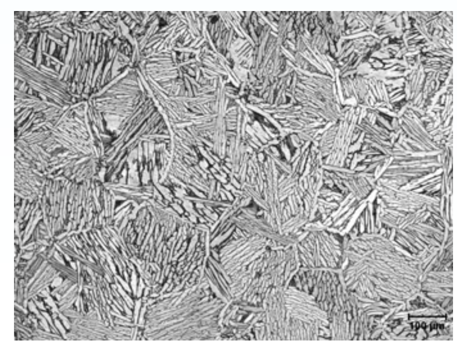
Extrusion

Sample Identification:	Ti-Grade 5
	%
Aluminum	6.26
Vanadium	4.4
Oxygen	.179
Iron	.077
Hydrogen	.0018
Carbon	.010
Nitrogen	.016
Manganese	.011
Total Others	<.4
Titanium	Balance

Low-oxygen P/M Ti-6Al-4V CIP/Sinter pre-forms produced from ADMA Hydrogenated Ti powder







Blended Elemental P/M Ti alloy Round Bars

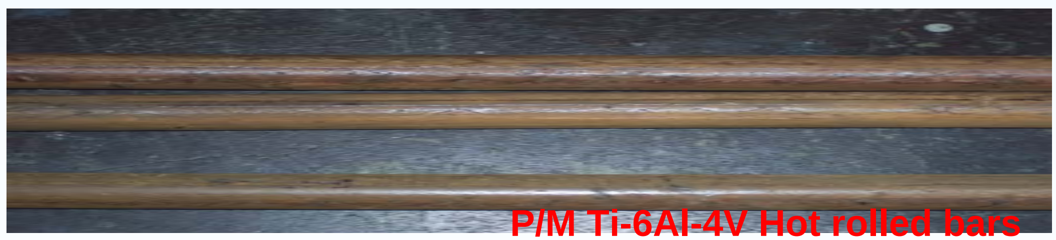
Cold Isostatic Pressing

Sintering

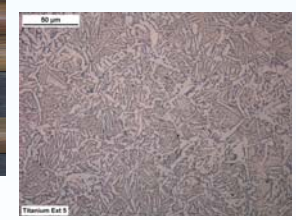
Extrusion | Rolling | Rotary Forging

P/M Ti-6Al-4V Extruded bars

P/M Ti-6Al-4V Rotary forged bars



P/M Ti-6Al-4V Hot rolled bars



P/M Ti-6Al-4V Extrusion billets

Ti-6Al-4V	Ultimate Strength, ksi	Yield Strength, ksi	Elongation, %	Reduction of Area, %
ADMA P/M	148 – 152	142 – 145	19.8 - 22.8	28.2 - 28.3
Ingot Based	140 - 143	125 – 127	19.4 - 21.1	26.9 - 27.6
AMS 4928R	135 Min.	125 Min.	10 Min.	

Conclusions

1. **Cost-effective process has been developed for manufacturing the hydrogenated titanium powder.**

2. **Manufacturing of hydrogenated titanium powder possessing desirable hydrogen and impurity content has been developed in Ukraine in cooperation with ADMA Products, Inc.**

3. **Cost-effective processes have been developed for the production of titanium alloy components from hydrogenated titanium powder.**

4. **Mechanical properties of powder metallurgy titanium alloys produced from hydrogenated Ti powder meet or exceed the requirements of ASTM and AMS specifications.**