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ORNL/TM-2012/534

Titanium Sheet Production from Commercial Powder

March, 2013

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UT-BATTELLE
ORNL-27 (4-00)

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ORNL/TM-2012/534

TITANIUM SHEET PRODUCTION FROM COMMERCIAL POWDERS

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Date Published: March 14, 2013

Prepared by
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Oak Ridge, Tennessee 37831-6283
Managed by
UT-BATTELLE, LLC
for the
U.S. DEPARTMENT OF ENERGY
Under contract DE-AC05-00OR22725

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LIST OF ACRONYMS

ARRA:	American Recovery and Reinvestment Act
AMO:	Department of Energy Advanced Manufacturing Office
AMS:	Aerospace Materials Standards
ASTM:	American Society for Testing and Materials
ASWRO:	Advanced Seawater Reverse Osmosis
CA:	California
CAP:	Campbell Applied Physics
CP-Ti:	Commercially Pure Titanium
CSIRO:	Commonwealth Scientific and Industrial Research Organization
CT:	Connecticut
CY:	Calendar Year
gpm:	Gallons per Minute
Gr:	Grade
GTAW:	Gas Tungsten Arc Weld
HDH:	Hydride-Dehydride
ICP:	Inductively Coupled Plasma
IL:	Illinois
in.:	Inches
ITP:	International Titanium Powder
kWh/m^3:	Kilowatt hour per cubic meter
MI:	Michigan
min.	Minute
MoU:	Memorandum of Understanding
NY:	New York
ORNL:	Oak Ridge National Laboratory
PA:	Pennsylvania
PM:	Powder Metallurgy
PM-Ti:	Powder Metallurgy Titanium
PR1:	Process Route 1
PR2:	Process Route 2
PR3:	Process Route 3
psi:	Pounds per Square Inch
RI:	Rhode Island
SEM:	Scanning Electron Microscope/y
T:	Temperature
TBtu:	Trillion British Thermal Units
$TiCl_4$:	Titanium tetrachloride
TiN:	Titanium Nitride
TN:	Tennessee
US:	United States
VIC:	Victoria (State of Australia)
W-Ti:	Wrought Titanium
ZrO_2:	Zirconium Dioxide

°C:	Degrees Celsius
°F:	Degrees Fahrenheit
ΔT:	Change in Temperature (Delta T)
// to RD:	Parallel to rolling direction
$\perp$ to RD:	Perpendicular to rolling direction
ε:	True strain
ν:	Kinematic viscosity

ACKNOWLEDGMENTS

This work was funded under the American Recovery and Reinvestment Act (ARRA) by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Advanced Manufacturing Office, under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

The authors would like to thank especially Dr. Yukinori Yamamoto for his expert microscopy, analysis, and phenomenological explanation of his observations; and Ron Swain for his professional service with mechanical testing.

The Authors would also like to thank David Hansard of Aqua-Chem for his willingness to both communicate Aqua-Chem's titanium needs and provide guidance in what material conditions would work for Aqua-Chem.

We would also like to thank Robert Campbell and his team at Campbell Applied Physics (CAP) for defining the need for flat titanium sheet and to advocate the need for an alternate supply chain for titanium. The test facilities and professional staff made available to accomplish the objectives of the program are most appreciated.

A heartfelt thank you is given to Muktesh Paliwal, Joe Capone and Ryan Smith of Ametek who as a team accomplished feed characterization and roll compaction work on the materials delivered in this project.

Thanks are also given to the industrial entities Niagara Specialty Metals and Solar Atmospheres, for timely work and coordination to meet schedule.

ABSTRACT

Powder metallurgy titanium sheet was produced from hydride dehydride (HDH) powder using a diverse industrial supply chain. Three different processing routes were developed and production protocols were established in each route to provide options for manufacturing sheet. The produced sheet was tested in accordance with American Society for Testing and Materials (ASTM) B265 specifications and found to be equivalent with grade 4 in yield strength and tensile strength and were at grade 2 levels for elongation. The produced sheet was tested in a newly designed flat plate heat exchanger specifically designed for enhanced reverse osmosis desalination. The powder metallurgy sheet was found to be equivalent in performance to commercially available sheet produced by the standard Kroll process. The testing allows for an alternate supply chain for thin gage titanium sheet to be developed that is not based on the often volatile, aerospace supply chain.

1. INTRODUCTION

The titanium industry came about by US Government funding in the late 1940's, to satisfy the need to produce sufficient quantities of titanium for aircraft, missiles, and spacecraft. Titanium rich ore was separated from oxygen by chlorination. The chloride was reduced to metal using batch chemical processing, and put into a useful form by vacuum melting and conventional wrought metalworking methods by a process that colloquially was named the Kroll process, after its inventor.[1] Processing costs were considered secondary to finished product output, resulting in poor material utilization, and associated high cost.

Recent developments in the production of low cost titanium powder from titanium chloride ($TiCl_4$), has the potential to enable a paradigm shift in the cost of production and application of titanium, if powder metallurgy fabrication techniques yield acceptable results.[2] Material utilization above 80% is feasible with fewer processing steps, less capital equipment, and lower energy needs. Titanium sheet costs are at least double other product forms, and low cost sheet would directly affect utilization in industrial applications for the chemical, petroleum, water purification, and heat exchangers markets.[3] Implementation of powder metallurgy technologies for sheet applications using the low cost titanium powders are required to take advantage of the cost savings. Thus far sheet produced from titanium powder in the laboratory shows promise. However, a sufficient fundamental understanding of the process variables to allow commercialization and scaling of the process are required before low cost titanium sheet components can be implemented.

This project targeted desalination heat exchangers plates (sheet) as a first step into commercial production of powder source sheet. The project was funded through the American Recovery and Reinvestment Act (ARRA) by the US Department of Energy Advanced Manufacturing Office (AMO). The tasks focused on determining process variables and controls on a laboratory scale and utilized that information to construct, on a limited basis, full sized heat exchanger plates, such that the maturation process to produce powder source sheet could be moved into commercial deployment at the end of the program.

1.1 POWDER SOURCING

Two titanium powder sources, hydride dehydride (HDH) from Kroll sponge, and Armstrong Process™ powder were identified as suitable for roll compaction into sheet. In the case of HDH powder, Global Titanium Inc., Detroit, MI, was the supplier. Cristal USA's, International Titanium Powder (ITP) division was the source for Armstrong Process ™ powders. At the time of project inception, ITP was commissioning a 2,000 ton per year plant in Ottawa, IL. The Armstrong Process ™ material was abandoned as a powder source, mid project, due to a lack of available powder. The making of sheet from powder metallurgy titanium for heat exchanger applications was performed only with HDH powder.

1.2 EQUIPMENT

To make the process of roll compaction to sheet commercially viable, it was the goal of this project to define the needed equipment in a semi-continuous process such that commercial integration would follow. Figure 1 shows a minimum equipment requirement and envisioned process schematic required to achieve fully consolidated titanium sheet.

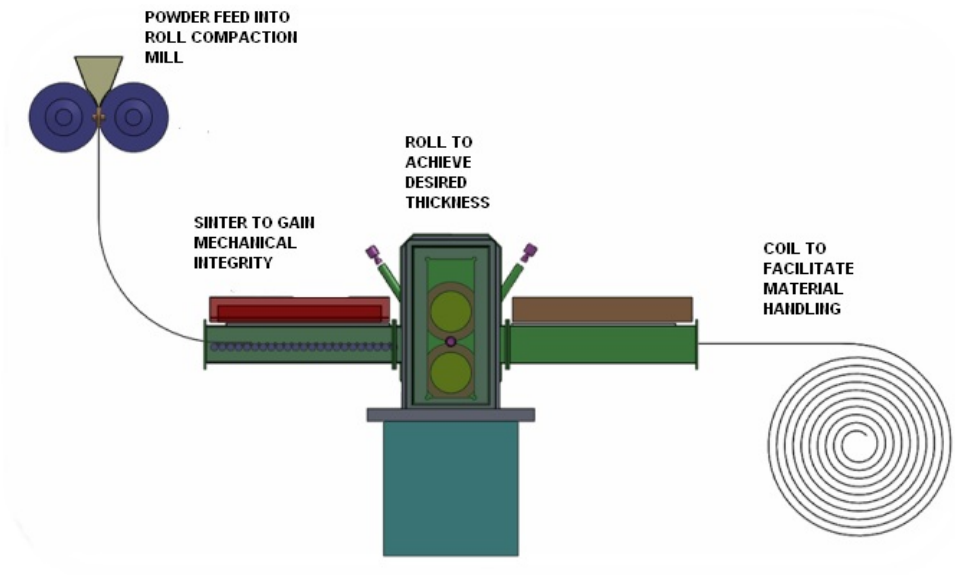


Figure 1: Schematic of the minimum process equipment required for roll compaction of titanium powder into sheet.

Two pieces of equipment; a roll compaction mill and a combination vacuum / inert gas hot rolling mill identified in the schematic were deemed to be required assets to facilitate completion of the work. A subcontract for retooling a used 7 inch wide roll compaction mill for use with titanium powders was issued to International Rolling Mills, Pawtucket, RI. Delivery delays and difficulty meeting the electrical requirements required a workaround to maintain project schedule. The mill was delivered and installed but was not used for this work due to the timing delays. Figure 2 shows the completed roll compaction mill, which is slated for use on subsequent projects. To accomplish the work on schedule, Ametek Specialty Metal Products, Wallingford, CT was contracted to perform the roll compaction work on existing equipment. Ametek met the required timing using a 15 inch wide production mill. Roll compacted titanium exiting Ametek's 15 inch wide mill is depicted in figure 3.

Figure 2: ORNL's 7 inch wide roll compaction mill with 17 inch diameter rolls.

Figure 3: Strip of roll compacted titanium exiting Ametek's 15 inch wide mill.

The vacuum / inert gas hot rolling mill was initially determined to be a custom built rolling mill. ORNL, as a cost saving measure, chose to retrofit an existing rolling mill for vacuum/ inert gas hot rolling service, to meet budget and time constraints. After writing a specification and going through a

formal bid and proposal process, the bid prices were outside the available budget. The inert hot mill project was abandoned and a workaround was developed utilizing hot rolling in a steel can. During the project it was discovered that the Commonwealth Scientific and Industrial Research Organisation (CSIRO), Clayton, VIC Australia was commissioning an inert hot rolling mill for titanium powder metallurgy sheet rolling. A memorandum of understanding (MoU) was signed between ORNL and CSIRO for collaborative research. The MoU allowed for sample quantities of sheet to be produced via the inert hot rolling mill at CSIRO; however quantities sufficient for heat exchanger testing were not available. Reporting on the advantages and challenges associated with inert hot rolling will be described in this document.

1.3 INDUSTRIAL PARTNERS

The project was conceived with the vision of being able to produce titanium powder metallurgy sheet with tensile elongations defined in *ASTM B265, Standard Specification for Titanium and Titanium Alloy Strip, Sheet, and Plate*.[4] Within the specification, Grade 2 commercially pure titanium (CP-Ti), with a minimum tensile elongation of 20% was the targeted objective for the powder metallurgy titanium (PM-Ti). Further the vision included partnering with Ametek Specialty Metal Products, Wallingford, CT a commercial manufacturer of powder metallurgy sheet from other metals and Aqua-Chem, Knoxville, TN a commercial manufacturer of salt water heat exchangers. The partnerships were intended to combine a new supplier of titanium sheet (Ametek), with an industrial entity that utilized conventional stamping operations to deform titanium sheet for use in heat exchangers (Aqua-Chem). During the course of the project Aqua-Chem became less involved as the promise of an acceptable new sheet source diminished, due to lower than expected sheet formability, higher than expected costs, and schedule delays. Campbell Applied Physics (CAP), Eldorado Hills, CA became a significant industrial partner in late CY 2010, replacing Aqua-Chem as an active partner. CAP's need was for a reliable source of thin gauge titanium (less than 0.01 in.) sheet for plate heat exchangers, to enhance flux in reverse osmosis desalination plants. CAP was not constrained by an existing heat exchanger design as was Aqua-Chem, and lower than expected formability was not relevant for CAP's needs. Powder metallurgy titanium (PM-Ti) sheet produced in this project was tested in a heat exchanger at CAP's facility in Eldorado Hills, CA at the close of this project, and found to be equivalent to Kroll processed, wrought, grade 2 titanium sheet.

2. PROJECT DETAILS

The process for consolidating titanium sheet from powder sources began by systematically characterizing the powder's physical and metallurgical properties, building on other titanium powder metallurgy work being performed at ORNL. Compositional analysis via inductively coupled plasma (ICP) for trace elements, and Leco interstitial analysis for hydrogen, oxygen and nitrogen were performed on feed materials. Scanning electron microscopy (SEM) was used to examine powder morphology. For HDH powders, size classification was not required and the powders were used in the as-received condition.

HDH powders required additives to be blended with the powders to achieve acceptable flowability during roll compaction. In addition to the flowability the additives were chosen to volatilize at a low temperature and leave minimal adverse residues that would degrade the titanium when subjected to sintering temperatures. Those additives were considered proprietary to Ametek, who performed the roll compaction work. In addition to the additives the feeding of powders correctly into the roll compaction mill to achieve consistent results is machine specific information, as is horsepower and torque requirements that define the compacted density, sheet thickness and sheet width. Ametek's 4 inch wide and 15 inch wide mills were used for this work, and specifics on the machines are retained as proprietary to Ametek. Results achieved on the materials that were roll compacted are presented in this work.

Once roll compaction was complete, thermal treatment to sinter the roll compacted sheet was accomplished. Due to the temperatures required and the reactivity of titanium at the required temperature, special processing was developed to avoid damaging the roll compacted metal.

Several processing routes, after sintering, yielded suitable sheet and those routes are described below. The processing routes were designed around existing industrial infrastructure, such that deployment was achievable when market pull warranted execution.

Produced sheet from one of the processing routes was configured into flat sheet for testing in a prototype heat exchanger at CAP. The testing was short duration giving only limited information however functional proof that PM-Ti sheet could be used for the application was demonstrated.

2.1 SPECIFICATION FOR SHEET

ASTM B265-11; *Standard Specification for Titanium and Titanium Alloy Strip, Sheet and Plate* is the recognized specification for wrought titanium sheet.[4] A summary of the composition and properties associated with the various grades of commercially pure titanium (CP-Ti) is taken from that specification and presented in Table 1. Within the specification, grade 2 is the dominant tonnage grade for industrial uses where a good balance between cost, strength, weldability, formability, and corrosion resistance exists. This work targeted reaching ASTM B265 Grade 2 properties, specifically elongation values using powder metallurgy consolidation methods.

Table 1: Composition and Mechanical Properties of Commercially Pure Titanium Taken from ASTM B265-11[4]

CP-Ti	Weight percent elements							Mechanical Porperties				
Grade	Carbon, max.	Oxygen max.	Nitrogen, max.	Hydrogen, max	Iron max.	Other elements max. each	Other elements max. total	UTS (ksi)	YS 0.2% offset (ksi) min.	max.	% elong 2 in. gl	Radius material thickness T, < 0.07
1	0.08	0.18	0.03	0.015	0.20	0.1	0.4	35	20	45	24	1.5T
2	0.08	0.25	0.03	0.015	0.30	0.1	0.4	50	40	65	20	2T
2H	0.08	0.25	0.03	0.015	0.30	0.1	0.4	58	40	65	20	2T
3	0.08	0.35	0.05	0.015	0.30	0.1	0.4	65	55	80	18	2T
4	0.08	0.40	0.05	0.015	0.50	0.1	0.4	80	70	95	15	2.5T

Three different processing routes achieved the stated objective of meeting ASTM B265 tensile elongation properties for grade 2 titanium; strengths were higher than that for grade 2 and fell within the grade 4 specification. Compositional limits were able to be maintained to grade 3 specifications. In addition to meeting the tensile elongation requirements of ASTM B265 grade 2 specifications, the mission of the project was to make powder metallurgy sheet suitable for an industrial heat exchanger. Aqua-Chem required highly formable sheet at 0.02 inches thick to deploy in their heat exchanger. The PM-Ti sheet produced by any of the three processing routes was not suitable for subsequent manufacturing by Aqua-Chem due to low formability and the relevance of the work waned. An explanation about the specification of titanium versus formability as it pertains to Aqua-Chem is discussed in Appendix A.

Campbell Applied Physics (CAP), a mid-project partner, had a need for a heat exchanger that could use 0.008 inch thick flat titanium, eliminating the need for highly formable sheet, but retaining the corrosion resistant properties of titanium. A heat exchanger was tested at CAP's facility in Eldorado Hills, CA using flat titanium powder metallurgy sheet, 0.008 inches thick. The sheet was found to be equivalent to commercial wrought titanium sheet in a limited, short duration test. The design of the test heat exchanger is proprietary; however the titanium sheet manufacturing method is described below.

2.2 CHARACTERIZATION OF FEED

HDH powder sources were chosen as candidate materials for consolidation into sheet via roll compaction. Several sources of HDH powders were used for process development and those compositions and characteristics are not presented, for brevity. Table 2 summarizes the composition of the HDH powder used for the final produced sheet.

Table 2: Composition and physical attributes of the HDH powder used in the consolidation work

		Global Ti HDH
Elements	Al (wt%)	<0.01
	V (wt%)	0.02
	Fe (wt%)	0.04
	Si (wt%)	<0.01
	Na (wt%)	<0.01
	Mg (wt%)	0.01
	C (wt%)	0.003
	S (wt%)	<0.001
	O (wt%)	0.0212
	N (wt%)	0.003
	H (wt%)	0.0133
	Ti	Bal
Sieve analysis	+80 (wt%)	0
	-8 +100 (wt%)	0
	-100 +140 (wt%)	10.06
	-140 +200 (wt%)	22.37
	-200 +270 (wt%)	20.73
	-270 + 325 (wt%)	6.75
	-325 (wt%)	40.09
	Apparent density	1.4 g /cm^3
	Bulk Density	1.53 g /cm^3
	Tap Density	1.88 g /cm^3
	BET (m^2 /g)	≈0.1
density at compaction pressures	5000 (psi)	
	10000(psi)	
	25000 (psi)	
	40000 (psi)	3.18 g/cm^3
	50000 (psi)	3.38 g/cm3
	60000 (psi)	3.56 g/cm3
	70000 (psi)	3.67 g/cm3
	80000 (psi)	3.76 g/cm3

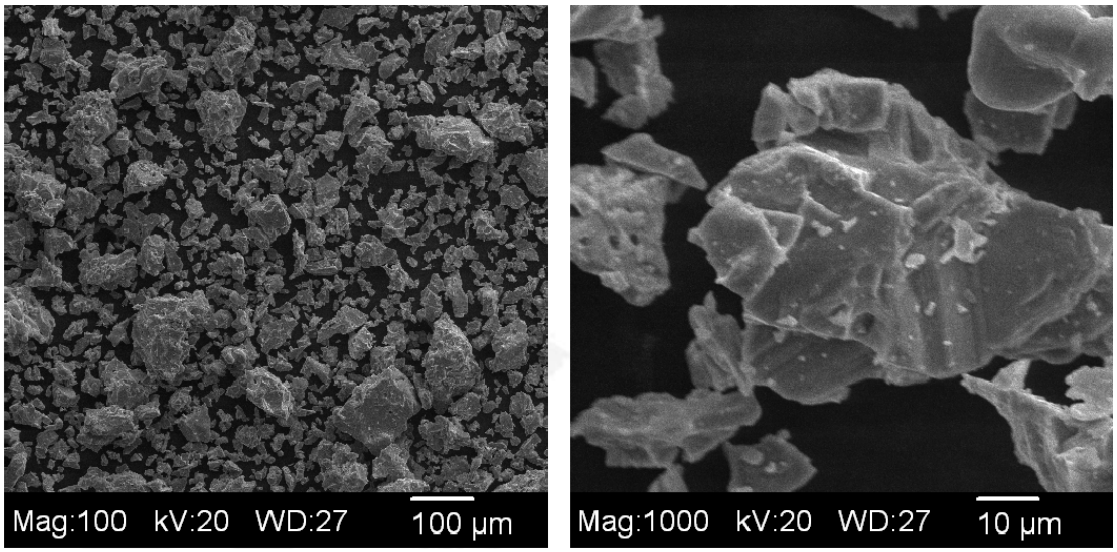


Figure 4: SEM images of Global Titanium's HDH powder used for roll compaction into heat exchanger plates in this study.

The blocky nature of the HDH powder (figure 4) gives the attribute of having greater than 30% natural bulk density and being flowable in the nip of a roll compaction mill; hence HDH powders require additives to control flow behavior during roll compaction.

2.3 ROLL COMPACTION / SINTERING

Roll compaction of Global Titanium's HDH powder was accomplished first on Ametek's 4 inch wide roll compaction mill, to determine feasibility, then, in sufficient quantity on the 15 inch wide production mill to produce 50 sheets of roll compacted strip measuring 15 inches by 30 inches by rolled thickness (approximately 0.1 to 0.12 inches). Roll compaction on the production mill was semi-continuous and strip exiting the mill had to be cut in 30 inch lengths to accommodate vacuum sintering. In the ideal situation continuous strip sintering, in an inert atmosphere furnace, directly after roll compaction, but prior to hot rolling, would represent an obvious production sequence. Such a furnace was not available for this work; therefore sintering was conducted as a batch operation.

Vacuum sintering was envisioned to be a two-step process. The first step was a low temperature cycle used to remove binder material from the green strip. The second step was a 1,100°C cycle to sinter the titanium sufficient for either cold or hot rolling.

The binder removal cycle was performed on the roll compacted sheets at Solar Atmospheres, Souderton, PA. A thin gauge stainless steel box with a labyrinth style loose fitting lid and a provision for an argon purge was fabricated, and was capable of holding 20 sheets of 15 inch wide by 30 inch long roll compacted sheet, spaced with ceramic insulators. The loaded box was placed inside a vacuum furnace and the furnace was evacuated to 1 x 10^{-4} torr (min.), backfilled with argon, evacuated a second time, backfilled a second time while applying low flow argon purge to the box. The furnace was heated at a rate of 2°C / min to a setpoint determined in the field. A thermocouple placed inside the box reached 300°C and a one hour hold at 300°C was performed, based on the in-box thermocouple reading. After the 1 hour hold, a high vacuum pumpdown was initiated followed by a 1 hour hold in vacuum. After the 1 hour vacuum hold, a low flow argon purge was initiated into the box to allow the vacuum chamber to run in a partial pressure of argon. During the 1 hour partial

pressure cycle, the box temperature was maintained at 300°C. Following the partial pressure cycle, another vacuum pumpdown was initiated with zero power applied to the furnace elements. The furnace was allowed to cool under vacuum conditions.

Trials to determine a strategy for sintering roll-compacted titanium sheet were attempted, with favorable results on single sheets and with unfavorable results with a stack of multiple sheets. Single sheet vacuum sintering trials at 900°C, 1,000°C, 1,100°C, 1,200°C, and 1,300°C were tested at subscale. The 1,100°C temperature was chosen based on the trials and was the minimum temperature where complete sintering of particle to particle contact points was observed with a 1 hour exposure time. There was a strong impetus to keep the sintering temperatures below 1,150 °C since production furnaces require a different design when temperatures above 1,150°C are required. {Vacuum furnaces suitable for titanium processing with temperature capabilities above 1,150°C, are typically made of refractory metals, have high maintenance intervals and are smaller in size.} 1,100 °C was deemed an acceptable value to accomplish sintering. To prevent titanium from reacting with the support fixturing during vacuum sintering ORNL used zirconia (ZrO_2) plates spray coated with titanium nitride (TiN) to support the titanium during the trials. No reaction was observed in single sheet trials.

For economy, graphite plates coated with zirconium oxide was the preferred spacing material between sheets in Solar Atmospheres' furnace. A single sheet supported on the graphite thus coated was acceptably sintered; however as the stack height increased and therefore the mechanical load on sheets near the bottom of the stack increased, the titanium stuck to the coated graphite, damaging the surface. Figure 5 shows the reaction points from interaction with the coating. Several coating combinations that had previously been acceptable at ORNL in early, single layer trials were attempted in multilayer trials under a load that mimicked what was predicted in the field. No coating combination was found to be acceptable in a multistack arrangement. Vacuum sintering of a multistack of titanium roll compacted sheet was abandoned.

The few single sheets of material that were successfully sintered at Solar Atmospheres were retained for further study at ORNL and some were subsequently sent to CSIRO for inert hot rolling trials. For the remaining 45 plates only a binder removal cycle was completed prior to hot rolling. An example of the roll compacted sheet being unpackaged and staged for hot rolling is depicted in figure 6.

Figure 5: Fifteen inch wide roll compacted sheet sintered at 1100°C in a multistack layer in contact with ZrO_2 coated graphite at 1,100 °C. A black reaction zone is apparent.

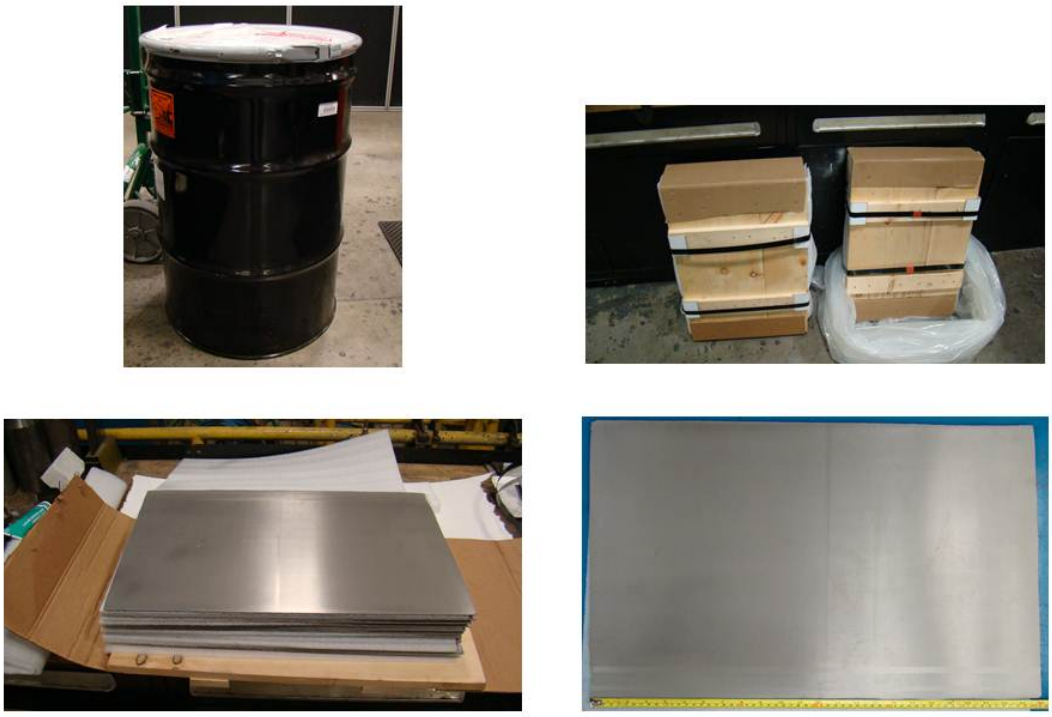


Figure 6: Sequence of photographs showing the packaging and surface finish of the roll compacted plates after binder removal.

2.4 THREE PROCESSING ROUTES TO PRODUCE SHEET

After binder removal, consolidation to fully dense sheet followed three primary processing routes. Processing route 1 was a multistep cold rolling / annealing route where sample quantities were produced for evaluation. Process route 2 was inert hot rolling at CSIRO, where again sample quantities were produced for evaluation. Process route 3 was hot rolling in a steel can in a multiple layer configuration, followed by cold rolling / annealing. Sufficient quantities of sheet to install in a heat exchanger were processed via process route 3, due to timing and available industrial infrastructure at the time of need.

The three methods were chosen based on an evaluation of the industrial infrastructure required to produce sheet currently, and also with consideration of building a unique manufacturing capability that would optimize the process as the markets expand.

A sheet thickness of 0.04 inches was chosen as the basis for all mechanical testing so that a consistent comparison between the various processing routes could be attained without the ambiguity of varying thicknesses in formability testing.

2.4.1 Process Route 1 (PR1)

Four vacuum sintering / cold rolling cycles were required to produce to produce 0.04 inch thick sheet for testing. The initial 1,100°C cycle, followed by three additional vacuum sintering cycles all performed at 1,100°C for 1 hour after a cold rolling progression. The average amount of true strain that was taken between sintering cycles increased as the material was rolled to thinner gages. The average target first stage of cold reduction was 25% true strain (ε). The second cold rolling progression accomplished 30% ε, and the third cold rolling reduction accomplished 35% ε. A final cold reduction to achieve a thickness of 0.042 inches varied from 5% ε to 15 % ε depending on starting roll compacted thickness. {The 0.042 inch target allowed for surface conditioning via grinding to be perfromed in the usual practice for titanium sheet.} After rolling to 0.042 inches a final anneal at 800°C for 1 hour was performed on the sheet to achieve desired mechanical properties,followed by grinding with a 320 grit wheel to achieve the desired 0.04 inch thick test sheet and produce the necessary surface condition used for titanium forming [5].

2.4.2 Process Route 2 (PR2)

As mentioned previously single sheets of 15 inch wide by 30 inch long roll compacted sheet from HDH powder that were successfully sintered at Solar Atmospheres were sent to CSIRO under an MoU agreement, for processing in CSIRO's inert hot mill.[6,7] The sheet required splitting into 7 inch widths to accommodate the furnace limits at CSIRO. The sectioned material was heated above 1,200°C and inert hot rolled in a single pass from 0.11 inches to 0.073 inches to densify the material. Following inert hot rolling the material was returned to ORNL for annealing and testing. Annealing after rolling and testing was ORNL's contribution to the MoU. Both as-rolled material and annealed material was ground to 0.04 inches with a 320 grit wheel to retain the consistent 0.040 thickness for comapritive testing between processing routes. The ground sheet was tested for composition, tensile properties and formability. {Grinding is a typical practice used in titanium sheet metal finishing to remove surface imperfections that negatively influence performance in service[8,9]. The excessive removal required here, to achieve the testing thickness of 0.04 was wasteful, but necessary for comparitive testing. In practice rolling would achieve a near finish gage, followed by annealing resulting in a rolled prodcut where between 0.001 to 0.0015 inches of surface removal would be

required to achieve properties. }The annealing cycle in PR 2 mimicked that of PR 1 i.e. 800°C for 1 hour in vacuum.

2.4.3 Process route 3 (PR3)

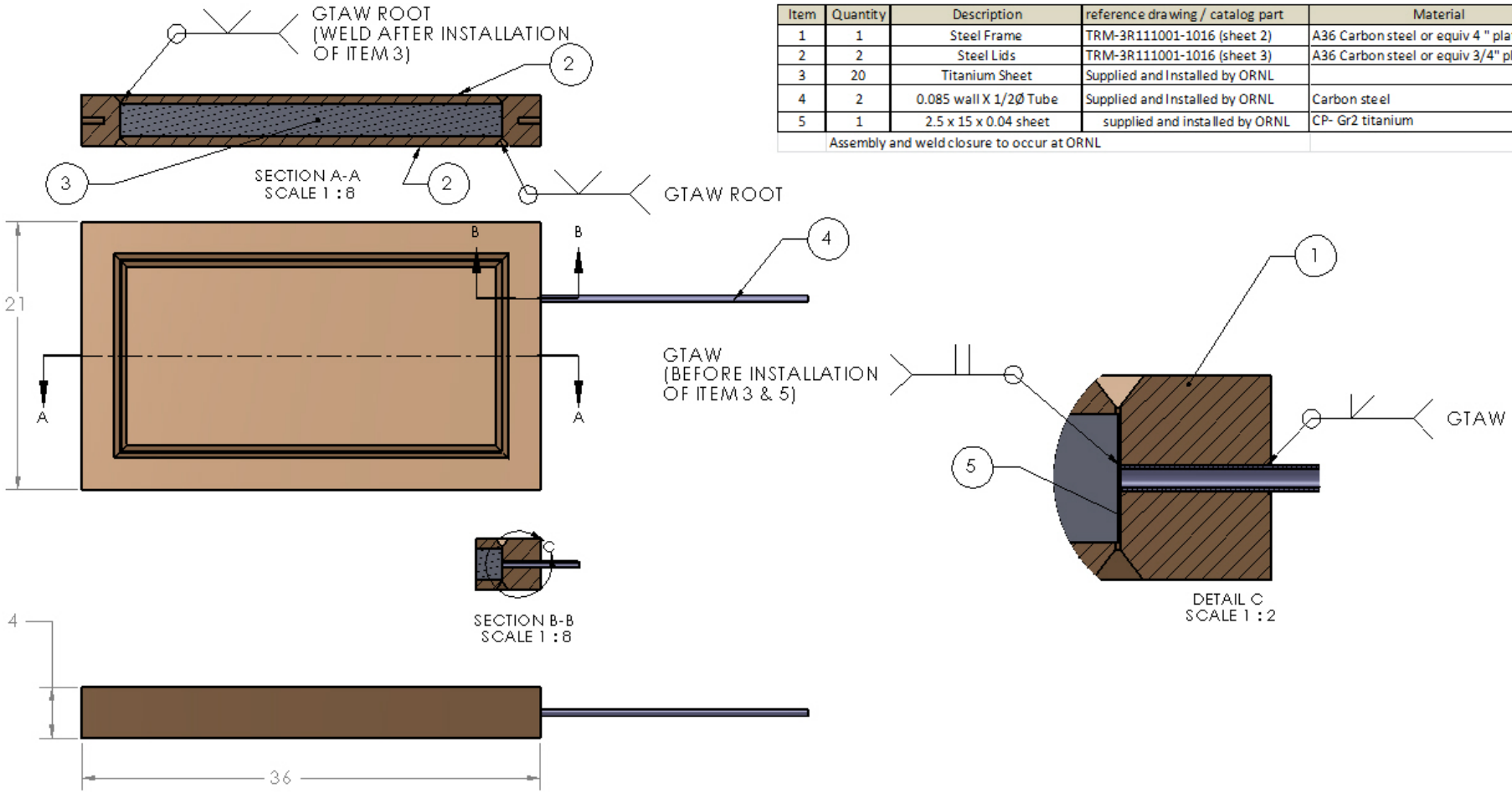
Twenty sheets of roll compacted HDH based powder metallurgy titanium sheet that had the binder removed with a low temperature vacuum / inert atmosphere bakeout, were loaded into a carbon steel can shown schematically in figure7. The can was deemed a suitable alternate to vacuum hot rolling whereby the atmosphere in the can could be controlled during the rolling process. The can was welded closed to seal the titanium inside. A tube was attached such that after weld closure an evacuation of the can could be accomplished. After can evacuation, a seal was accomplished by crimping and welding the tube. Figure 8 is a photograph of the steel can taken during the loading process.

Hot rolling of the steel can was accomplished at Niagara Specialty Metals, Akron NY. A schematic of the rolling strategy is shown in figure 9. Table 3 depicts the target rolling schedule. Field conditions during hot rolling required some changes to be made to the schedule, but the general guidelines are reflected in the Table. At the ½ inch thickness the carbon steel can was detached from the titanium and hot rolling of the titanium was completed in the absence of the steel can (bare rolling). The steel can was sufficient to allow consolidation of the roll compacted sheets during the first two stages of hot rolling, and bare rolling took place with no adverse effects. The yield from hot rolling was 8 sheets of hot rolled titanium approximately 0.06 inches thick by 15 inches wide by 70 to 80 inches long. The hot rolled sheet was annealed and creep flattened in an air furnace at 800°C for 1 hour. Following annealing, a single sheet to be used for testing was ground from 0.060 to 0.040 on a belt type grinding machine at Niagara's facility. The remaining seven sheets plus remnant scrap was stored for further processing pending, a compositional examination, tensile testing and formability testing.

Test results on material processed via PR3 were sufficiently encouraging to commit 4 of the seven, 70 inch long sheets to further processing. Four pieces were ground from a rolled thickness of approximately 0.06 inches to 0.04 inches to remove hot roll scale, alpha case and any imperfections caused by handling. The grinding took place under subcontract to Specialty Metals Processing, Inc., Stow OH and was accomplished on a grinder specifically designed for titanium.

Figure 10 is a summary flow sheet of the 3 processing routes with compsotional testing and mechanical property testing accomplished on all 3 routes at a a thickness of 0.04 inches. Further rolling of processing route 3 material was required to meet the designe requirements of CAP's heat exchanger.

Following grinding, two cold rolling sequences to reach a final rolled thickness of 0.008 inches were performed on ORNL's 4-high cold rolling mill depicted in figure 11. An intermediate anneal at 800°C for 2 hours after rolling to a thickness of 0.02 inches was perfromed to recrystallize sheet and return sufficient ductility to allow further rolling. The final sheet at 0.008 inches thick was left in the as-rolled condition for testing in a heat exchanger.



Item	Quantity	Description	reference drawing / catalog part	Material
1	1	Steel Frame	TRM-3R111001-1016 (sheet 2)	A36 Carbon steel or equiv 4 " plate
2	2	Steel Lids	TRM-3R111001-1016 (sheet 3)	A36 Carbon steel or equiv 3/4" plate
3	20	Titanium Sheet	Supplied and Installed by ORNL	
4	2	0.085 wall X 1/2Ø Tube	Supplied and Installed by ORNL	Carbon steel
5	1	2.5 x 15 x 0.04 sheet	supplied and installed by ORNL	CP- Gr2 titanium
	Assembly and weld closure to occur at ORNL			

Figure 7: A schematic diagram of the carbon steel rolling can.

Figure 8: Loading of the carbon steel can with roll compacted titanium sheet

2.4.4 Property Comparison and Interpretation of Results

Tensile testing was performed on materials from all three process routes and compared to Aerospace Materials Standards (AMS) 4900L, AMS 4902G, and ASTM B-265. Formability testing using a Tinius Olson Ductometer was carried out on each process lot as a qualitative test comparing load and dome height at failure with that for commercial aerospace grade 2 wrought titanium sheet that complied with both the AMS, and ASTM specifications. Compositional analysis to determine oxygen, nitrogen and hydrogen content of the processed sheet was also performed. The compositional evaluation was to determine interstitial element contamination levels attributable to processing.

All three processing routes showed tensile properties comparable to one of the grades of titanium in either AMS or ASTM specifications, as can be seen in Table 4. Table 4 also shows the composition of the sheet after processing as well as tensile properties and dome height test results. PR3 showed an increase in both oxygen and hydrogen during processing that was attributable to adsorbed water remnant in the steel can and on the multiple sheets prior to weld closure of the steel can. Comparing the results in the Table reveals that tensile elongation variations expectedly track with residual oxygen and nitrogen contents i.e. higher oxygen / nitrogen levels equate higher strengths and to diminished elongation.

Conventional wisdom holds that tensile ductility is a good proxy for formability, however testing proved otherwise. The formability tests summarized in Table 4 show dome height and load at failure for each of the three processing routes. These values are compared with those obtained from commercial wrought aerospace grade material. The powder metallurgy sheets show lower dome heights than aerospace grade, and the formability does not track with tensile elongation. A microstructural evaluation reveals some causal factors for low formability.

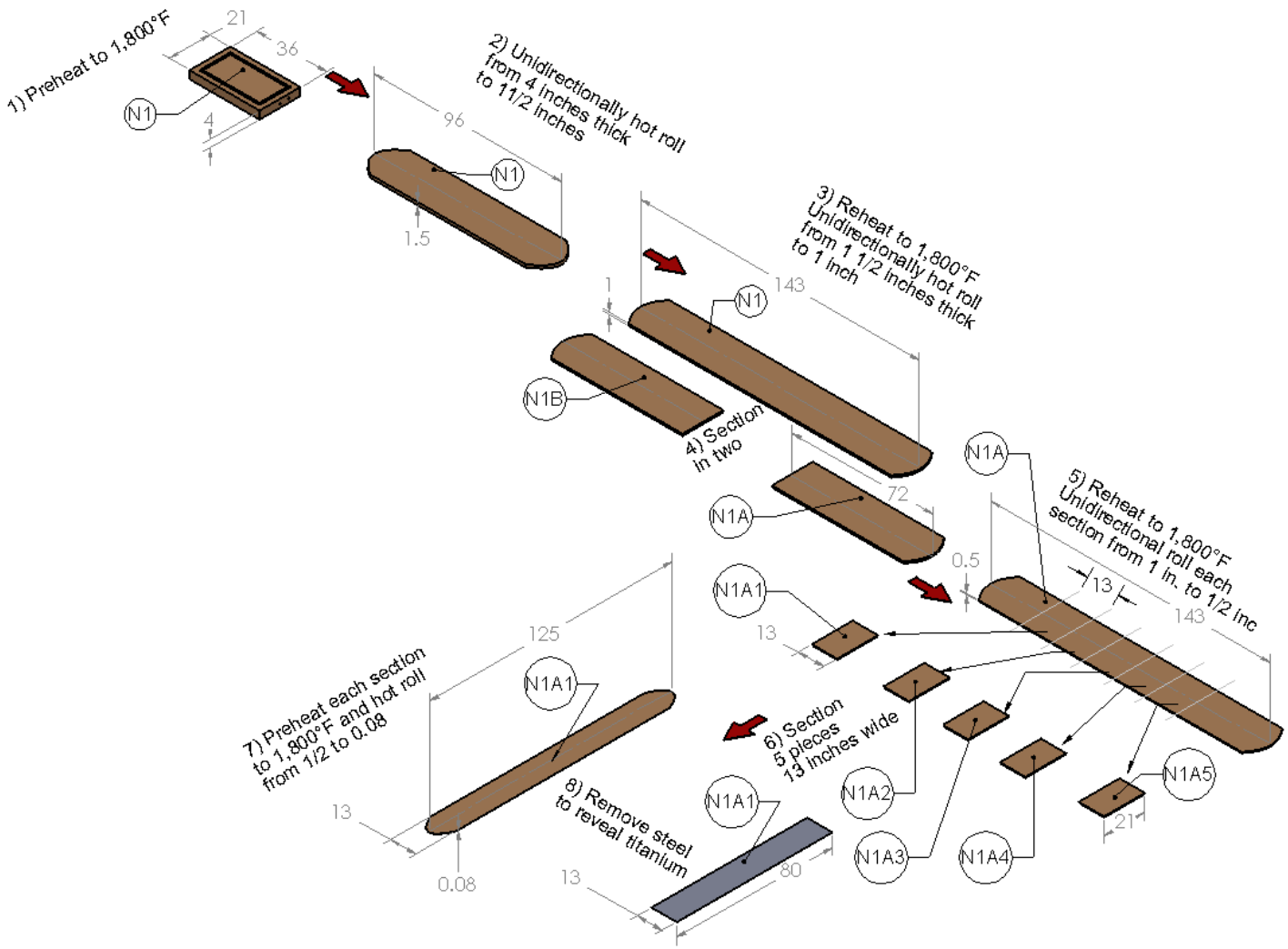


Figure 9: A schematic of the rolling sequence used for hot rolling the roll compacted titanium sheet in a steel can.

Table 3: Target rolling schedule for hot rolling roll compacted titanium sheet in a steel can

Heat	1800°F							
Pass	Prepass thickness	Prepass length	desired True strain per	Desired Mill set	Actual Mill Set	Estimated Length Strain	Estimated Thickness strain	Estimated Post Pass thickness
1	4	36	-0.05	3.805	3.805	37.846	0.05	3.80
2	3.8	37.8	-0.075	3.530	3.530	40.800	0.07	3.53
3	3.53	40.8	-0.1	3.194	3.194	45.100	0.10	3.19
4	3.19	45.1	-0.1	2.890	2.890	49.800	0.10	2.89
5	2.89	49.8	-0.12	2.563	2.563	56.200	0.12	2.56
6	2.56	56.2	-0.12	2.273	2.273	63.300	0.12	2.27
7	2.27	63.3	-0.12	2.016	2.016	71.400	0.12	2.01
8	2.02	71.4	-0.15	1.735	1.735	83.000	0.15	1.74
9	1.74	83	-0.15	1.494	1.494	96.400	0.15	1.50

Reheat	1800°F							
Pass	Prepass thickness	Prepass length	desired True strain per	Desired Mill set	Actual Mill Set	Estimated Length Strain	Estimated Thickness strain	Estimated Post Pass thickness
10	1.5	96	-0.2	1.228	1.228	117	0.20	1.23
11	1.23	117	-0.2	1.007	1	143	0.21	1.01

Cut into two pieces ≈ 72 inches long

Reheat pieces	1800°F							
Pass	Prepass thickness	Prepass length	True strain per	Desired Mill set	Actual Mill Set	Estimated Length Strain	Thickness strain	Post Pass thickness
12	1.01	72	-0.2	0.827	1.228	88	-0.20	0.83
13	0.82	88	-0.25	0.639	1	113	-0.20	0.64
14	0.64	113	-0.25	0.498	1	145	-0.45	0.50

Cut into 5 good piece ≈ 13 inches wide

Reheat pieces	1800°F	Roll- reheating as needed to keep pieces above 1100°F						
Pass	Prepass thickness	Prepass length	desired True strain per	Desired Mill set	Actual Mill Set	Estimated Length Strain	Estimated Thickness strain	Estimated Post Pass thickness
16	0.5	21	-0.25	0.389	0.39	27	0.25	0.39
17	0.39	27	-0.25	0.303	0.3	35	0.26	0.30
18	0.30	34.6	-0.25	0.236	0.236	44	0.25	0.24
19	0.24	44.5	-0.27	0.180	0.18	58.2	0.54	0.18
20	0.18	58.2	-0.27	0.138	0.138	76.3	0.41	0.14
21	0.14	76.3	-0.25	0.107	0.107	98	0.32	0.11
22	0.11	98	-0.25	0.083	0.083	125.8	0.25	0.08

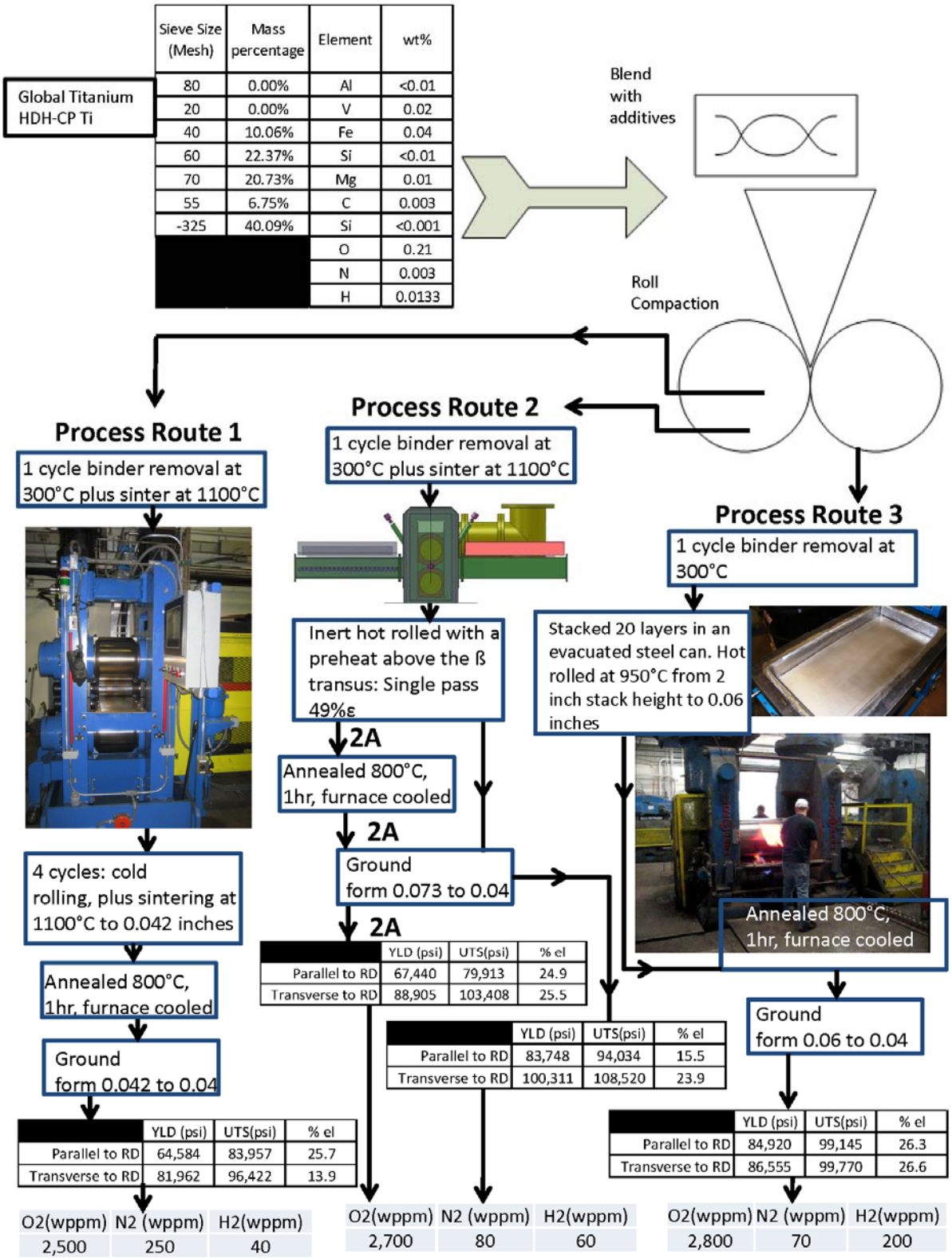


Figure 10: Schematic flow sheet for the 3 processing routes followed in this study

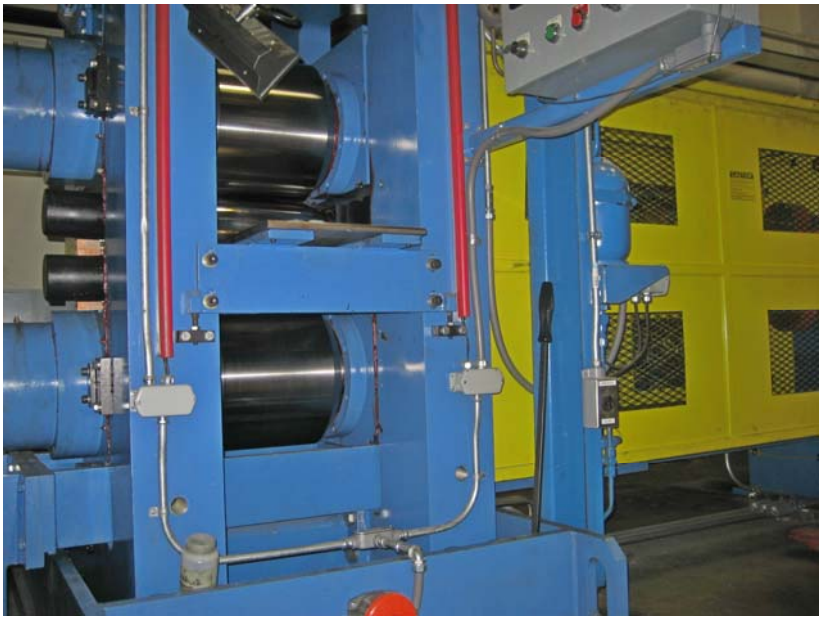


Figure 11: ORNL's 4-High rolling mill used for cold rolling of the PM titanium sheet

Figure 12 compares the microstructures of aerospace grade 2 wrought titanium sheet, with the microstructures of the three powder metallurgy titanium sheets processed by the different routes. The grain size of PR1, PR2 and PR3 are qualitatively similar to the aerospace grade material, however voids, predominantly at grain boundaries can be observed in PR1 material, and to a lesser extent in PR3 material. As can be seen in Table 3, the voids do not significantly reduce tensile elongation since PR1 has the highest tensile elongation of the three routes, and the highest fraction of visible voids. However the voids are a likely contributor to low biaxial formability where PR1 has the lowest dome height at failure; 0.09 inches. The microstructure of PR2 shows a typical equiaxed grain structure expected from annealing PR2 source material at 800°C for 1 hour. No discernible voids are observed in PR2 and formability is the highest of the processing routes.

An effort was made to take the produced sheet from PR1 and PR3 and make subscale herringbone / dimple patterns via stamping in accordance with Aqua-Chem's need. A typical full size heat exchanger plate is shown in figure 13a, with test coupons produced in subscale tooling in figure 13b. Tests were run at room temperature, and 300°C in air and 600°C in vacuum. The room temperature formability on sheet produced from PR3 material was limited as can be seen in the room temperature test coupon of figure 13b, where cracks are visible at the root of the herringbone channel, as well as the apex of the dimples. At 300°C the herringbones are sound however the dimples show thru cracking. At 600°C there is good formability with no observed cracking. PR1 material was also tested and found to be equivalent to PR3. PR2 was not tested due to schedule and timing limits associted with receipt of PR2 from CSIRO. The improvement in formability at elevated temperature on PR1 and PR3 is outside of AquaChem's normal process. The need for AquaChem is for the powder metallurgy titanium sheet to follow the normal course of production where both stainless steel and titanium are stamped at room temperature in the same press tooling. A tooling and process change to accomodate powder metallurgy titanium is untenable. AquaChem cannot yet use the available powder metallurgy titanium sheet. Campbell Applied Physics on the other hand did not have the

Table 4: A summary of the properties achieved with HDH roll compacted titanium sheet along with the ASTM standard properties[4]

		0.2% offset yield (psi)	UTS (psi)	% Elongation	Bend	*Dome heigth in biaxial test (in)	C max (wt%)	O max (wt%)	N max (wt%)	H (wt%)	Fe max (wt%)	OE (max) each	OE (max) total
PR1 HDH-Sintered Cold Roll x 5 Annealed	// to RD	84,989	99,202	26.3	2T	0.090	0.028	0.25	0.025	0.004	0.077		
	⊥ to RD	86,584	99,782	26.6									
PR2 HDH-Sintered Inert hot rolled annealed	// to RD	67,440	79,913	24.9	2T	0.420	0.014	0.27	0.008	0.006	0.049		
	⊥ to RD	88,905	103,408	25.5	2T								
PR3 HDH-Hot rolled annealed (steel can)	// to RD	64,584	83,957	25.7	2T	0.310	0.014	0.28	0.007	0.02	0.054		
	⊥ to RD	81,962	96,422	13.9									
ASTM B265 Gr 2		40,000 / 65,000 (min / max)	50000 (min)	20	2T	0.507	0.08	0.25	0.03	0.015	0.3	0.1	0.4
ASTM B265 Gr 3		55,000 / 80,000 (min /max)	65,000 (min)	18	2T	ND	0.08	0.35	0.05	0.015	0.3	0.1	0.4
ASTM B265 Gr 4		70,000 / 95,000 (min /max)	80,000 (min)	15	2.5T	ND	0.08	0.4	0.05	0.015	0.5	0.1	0.4

* Not specified in ASTM B265 but presented for comparison

contraints required by AquaChem and could accommodate a flat titanium sheet.; hence the focus turned to determining the suitablity of the PM-Ti sheet for application in CAP's heat exchanger.

Applications for the finished sheet are continuing to be examined by the ORNL led team, and are directed at applications for sheet below 0.04 inches in thickness where formability is not critical. Processing by PR2 requires an industrial investment in new equipment to be commercially viable, but has the advantage of potentially being a continuous process, with favorable economies.

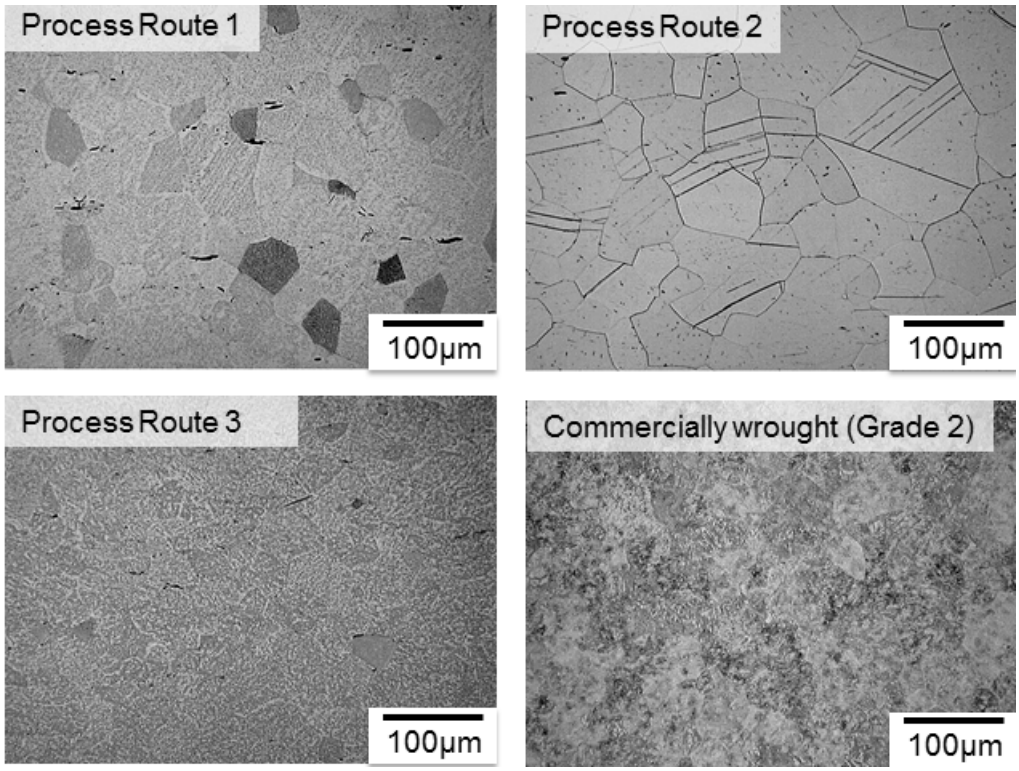
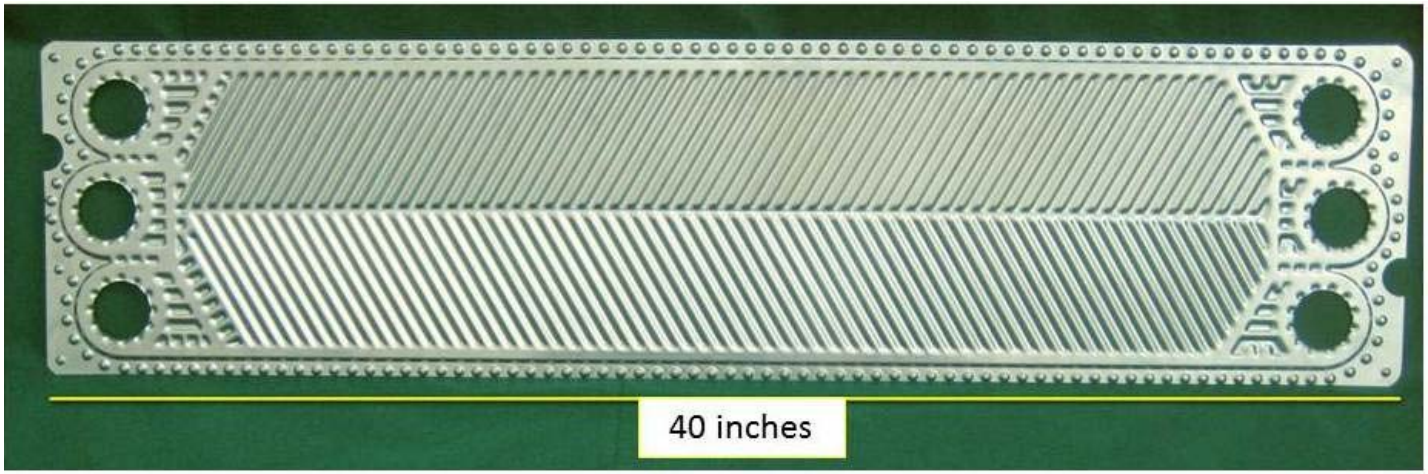
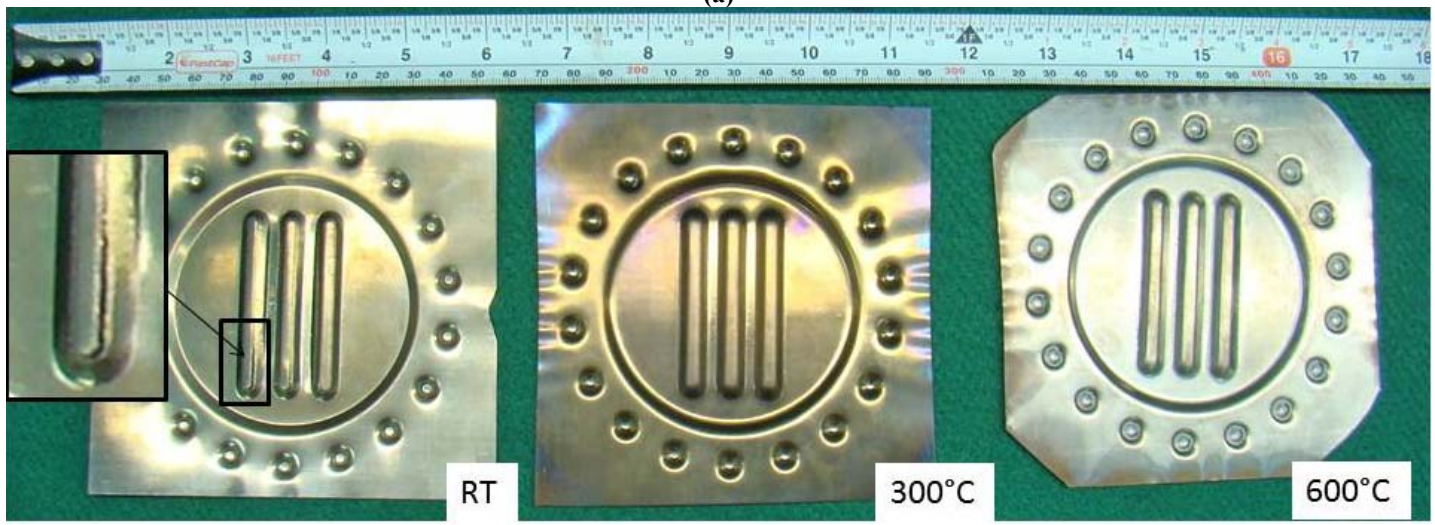


Figure 12: Optical micrographs of the rolled and annealed PM titanium, processed by the various processing routes and compared with commercial wrought metal.



(a)



(b)

Figure 13: Stamped conventional heat excahnger sheet is shown in (a), revealing the intricate herringbone and dimple pattern required. (b) shows the coupons produced at ORNL that were designed to mimic the required formability for the conventional sheet showing a lack of formability at room temperature (RT), improved formability at 300°C and excellent formability at 600°C in vacuum.

2.5 HEAT EXCHANGER TESTING

The heat exchanger used in this evaluation was a custom-designed three fluid cross flow flat plate design used to heat seawater from 15°C to 35 °C at a flow rate of 8 gallons per minute. The heat sources for the seawater were two seperate flows one of brine at 5 gallons per minute and 37°C and the other permeate (fresh water) at 3 gpm and 47°C. A schematic of the titanium sheet is depicted in figure 14. Figure 15 shows the actual sheet staged for installation in the heat exchanger. Figure 16 is a photograph of the heat exchanger in the test bay at Campbell Applied Physics (CAP).

Flowrates on the prototype heat exchanger were below designed target values and future tests would require a slight modification to the pumping and distribution system to achieve target flow. However, the dimished flows were consistent for each of the two metals tested; HDH, PM-Ti sheet and Kroll processed wrought sheet. Table 5 compares the test data showing that the change in temperature and pressure associated with the two different materials is at parity. Figure 17 is a graph depicting the response time and temperatures achieved with the two different materials in the test heat exchnager. Steady state temperatures were achieved in less than 2 minutes. The target temperature for outgoing seawater was 35°C. Figure 17a shows that PM-Ti was slightly better than wrought titanium, at achieving the 35°C target, however the permeate started at 1.5°C hotter than in the test with wrought titanium and accounts for the apparent improvement. Examining the change in temperature (**ΔT)** as referenced to the starting temperatures of the 3 input fluids (figure 17b); reveals a good match between the two different metal sources. Seal boundaries were preserved, no leaks were detected, thermal equivalency between the two metals was concluded. Dissasembly after testing revelaed no noticible corrosion, or other abnormalities. The conclusion was that PM titanium sheet is equivalent to wrought titanium sheet for this salt water heat exchanger application in the short duration test. Longevity testing is planned in follow-on work.

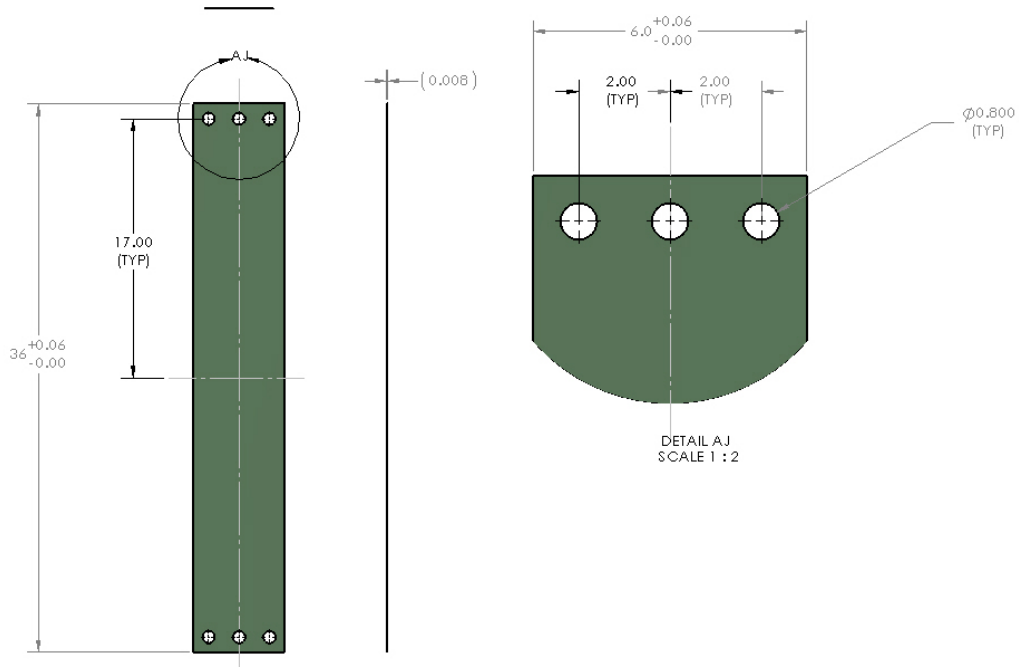


Figure 14: Schematic of flat Ti sheet for CAP heat exchanger

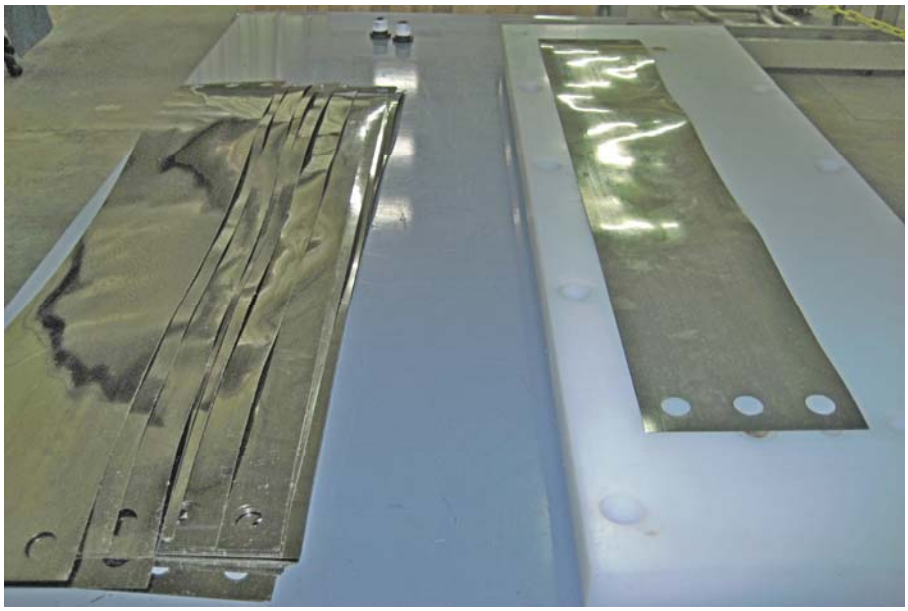


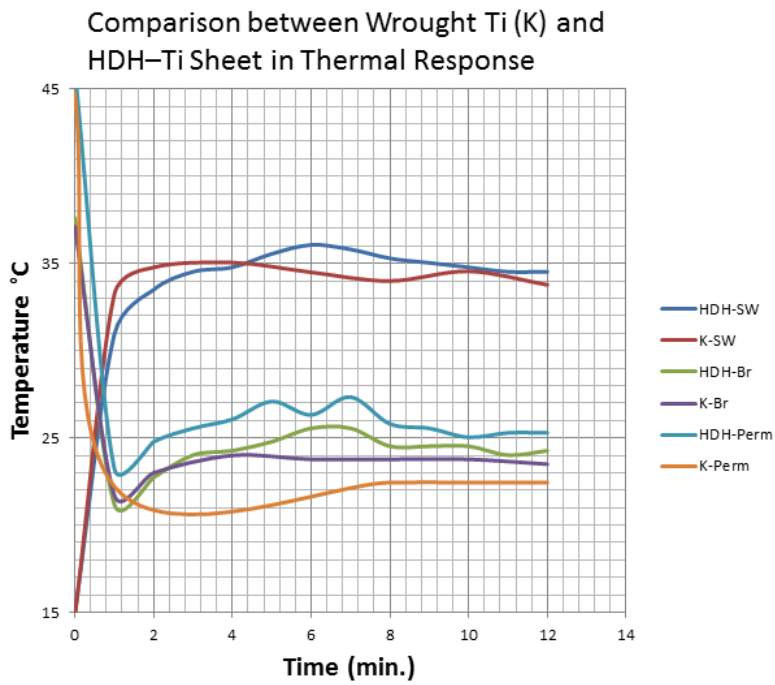
Figure 15: Cut, 0.008 inch thick, PM-Ti sheet staged for installation in the CAP heat exchanger.

Figure 16: 3-flow heat exchanger in the test bay at CAP

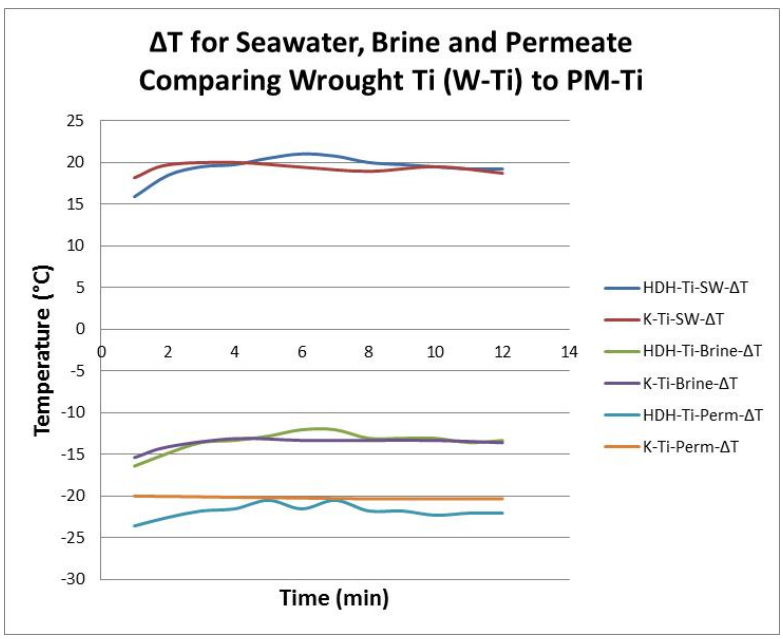
Table 5: A summary of the temperatures and pressures seen with Kroll based titanium and PM titanium showing thermal equivalency during heat exchanger testing

PM-Ti												
time	Seawater				Brine				Permeate			
	T_{IN}°C	T_{OUT}°C	ΔT (°C)	ΔP	T_{IN}°C	T_{OUT}°C	ΔT (°C)	ΔP	T_{IN}°C	T_{OUT}°C	ΔT (°C)	ΔP
0	15.0				37.6				46.1			
1	15.0	30.9	15.9		37.6	21.2	-16.4		46.8	23.2	-23.6	
2	15.0	33.5	18.5		37.6	22.7	-14.9		47.3	24.8	-22.6	
3	15.0	34.5	19.5	35	37.6	24.0	-13.6	30	47.3	25.6	-21.8	35
4	15.0	34.8	19.7		37.6	24.3	-13.3		47.6	26.1	-21.5	38
5	15.0	35.6	20.5	40	37.6	24.8	-12.8		47.6	27.1	-20.5	
6	15.0	36.1	21.0		37.6	25.6	-12.1		47.9	26.3	-21.5	
7	15.0	35.8	20.8		37.6	25.6	-12.1		47.9	27.3	-20.5	
8	15.3	35.3	20.0		37.6	24.5	-13.1		47.6	25.8	-21.8	
9	15.3	35.0	19.7		37.6	24.5	-13.1		47.3	25.6	-21.8	
10	15.3	34.8	19.5		37.6	24.5	-13.1		47.3	25.0	-22.3	
11	15.3	34.5	19.2		37.6	24.0	-13.6		47.3	25.3	-22.1	
12	15.3	34.5	19.2		37.6	24.3	-13.3		47.3	25.3	-22.1	

Wrought Ti												
Time (min)	Seawater				Brine				Permeate			
	T_{IN}°C	T_{OUT}°C	ΔT (°C)	ΔP	T_{IN}°C	T_{OUT}°C	ΔT (°C)	ΔP	T_{IN}°C	T_{OUT}°C	ΔT (°C)	ΔP
0	14.8				36.8				44.8			
1	15.1	33.2	18.2	42	37.1	21.7	-15.4	36		22.2		42
2	15.1	34.8	19.7	36	37.1	23.0	-14.1	32				36
4	15.1	35.1	20.0		37.1	24.0	-13.1					
6	15.1	34.5	19.4		37.1	23.8	-13.3					
8	15.1	34.0	18.9		37.1	23.8	-13.3			22.4	-20.3	
10	15.1	34.6	19.5		37.1	23.8	-13.3			22.4	-20.3	
12	15.1	33.8	18.7		37.1	23.5	-13.6			22.4	-20.3	



(a)



(b)

Figure 17: Comparison between wrought titanium and powder metallurgy titanium sheet in a heat exchanger test. Equivalent temperatures were achieved between the two metal as depicted in (a). Equivalent temperature differentials were achieved as depicted in (b).

3. BENEFITS ASSESSMENT

Energy and water are inextricably linked. Water is integral to energy generation, and vast amounts of energy are consumed in treating and moving water. Population growth is making clean, useable water an ever more precious and valuable resource. One seventh of the world's population lives in a distressed water condition and a significant portion are located next to the ocean and seas.[10] Desalination will be needed to fulfill an increasing proportion of the world's clean water needs. About 98% of the earth's water resources are brackish or seawater. Worldwide installed capacity for desalination of seawater is projected to be 120 million cubic meters per day by 2016. However, desalination is energy-intensive for fresh water production. Campbell Applied Physics has developed a desalination technology that reduces the average energy consumption of reverse osmosis from the current 3kWh/m^3 average down to 1.8kWh/m^3; a 40% reduction. The energy reduction comes largely from enhancements that are enabled by a titanium heat exchanger for the return of thermal energy back into the system.

Incoming seawater requires less energy to pump if the temperature is increased due to a drop in kinematic viscosity. The kinematic viscosity relationship is approximated by logarithmic plot with temperature shown in figure 18[11]. The equation $\nu = 2.8\ln(T) + 18.4$ (where ν = kinematic viscosity, and T= absolute temperature) is an approximation for the relationship of viscosity with temperature for average seawater.

Osmotic pressure has a linear relationship with the absolute temperature for a given total dissolved solids as depicted in figure 19 [12], that counteracts the energy benefits of lower viscosity. As the temperature increases higher pressures are required to achieve the same separation fraction of permeate to brine. For CAP, a nice balance is achieved at 35°C. Moderately deep seawater intakes typically have sea water at 15°C or colder. To achieve a near optimal energy utility for CAP's system, incoming seawater is coarse filtered, heated to 35 °C, ozonated for sterilization, pressurized via pumping to accomplish the RO separation of permeate and brine. Depending on local factors in the oceans for dissolved solids levels the separation generates 30% to 45% permeate at low pressure and 70% to 55% brine at high pressure. The heated brine carries a substantial amount of energy both from pressure and heat. A pressure exchange device is used for pressure recovery; recycling the pressure back into the new incoming seawater. The titanium heat exchanger is used to recycle the heat from the brine back into the incoming seawater. The efficiency of the heat exchanger and its longevity are key attributes for the energy savings. In addition to recycling the thermal energy from the heated brine, the produced permeate at 35°C is further used to cool process equipment whereby it increases in temperature to 44°C. The warm permeate's thermal energy is also delivered back to the incoming seawater through the same titanium heat exchanger, before being delivered as potable water. Titanium is the only identified common metal that has the necessary life-of-plant durability (25 plus years) for this technology. In today's desalination facilities, the addition of a titanium heat exchanger would save over 50 TBtu's. The vision of CAP is to have a domestically produced, readily available, low cost, heat exchanger with a life-of-plant durability to accomplish the energy savings.

CAP has projected a need in the next 2 to 3 years for 100 tons of titanium sheet, less than 0.01 inches thick for use in water purification technology.

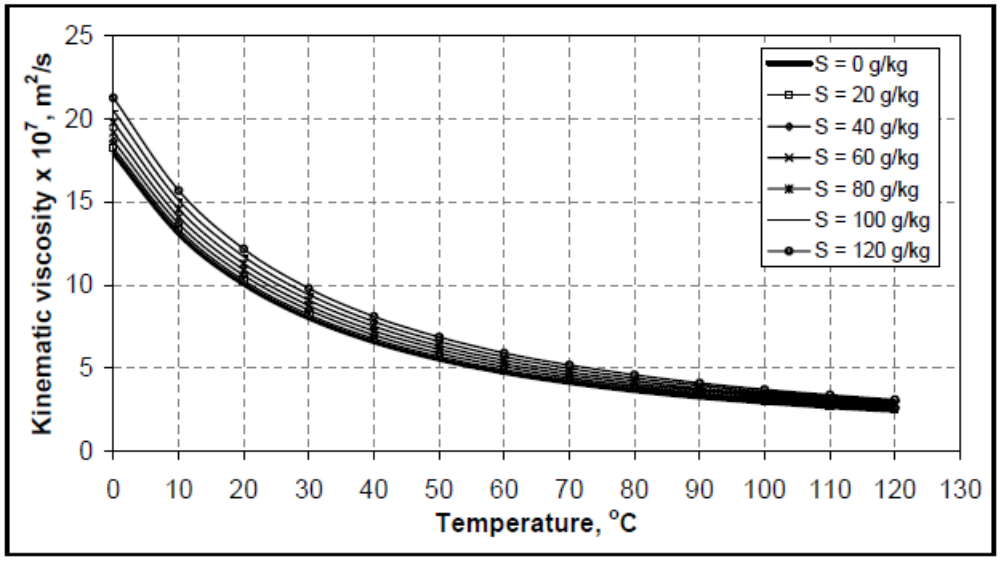


Figure 18: Kinematic viscosity change with temperature for seawater.[11]

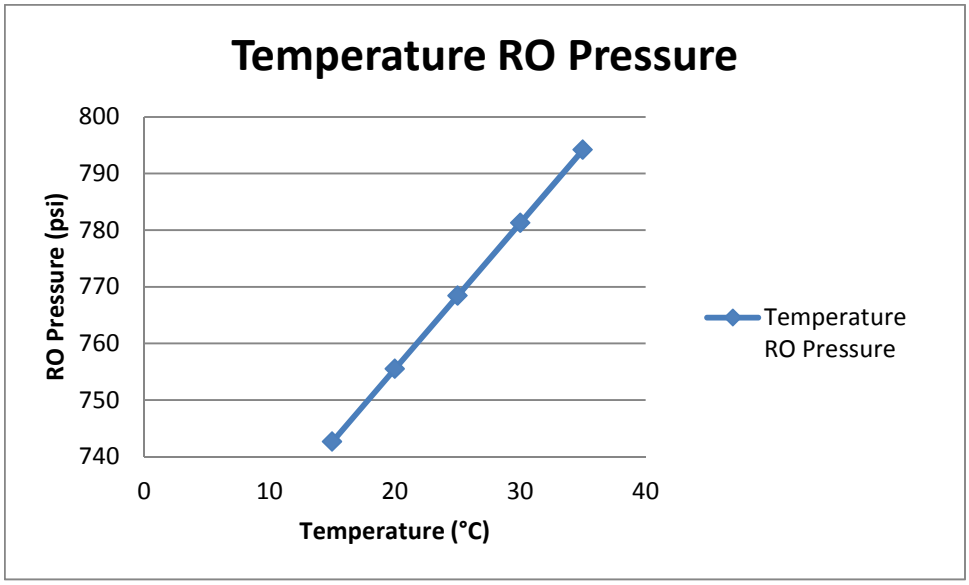


Figure 19: Relationship of temperature versus RO pumping pressure for "typical" seawater

4. COMMERCIALIZATION

Ametek has the infrastructure and knowhow to perform the powder blending of additives, accomplish roll compaction into green sheet and consolidate the sheet after sintering via cold rolling, Sintering is a missing capability at Ametek. During this work Ametek found suitable, commercially available sintering furnaces that can be purchased, should a profitable market develop for powder metallurgy titanium sheet. Two proprietary aspects of roll compaction of HDH titanium that are retained by Ametek are 1) the formulation of addtives necessary to achieve flowability while not spoiling the product titanium upon vacumm sintering and 2) feeding technology devloped over years of producing other PM alloy sheets. It is essential to consistently feed the powder into the nip of the roll compaction mill to achieve a uniform thickness and density across the width of the sheet. Other sources of roll compacted titanium sheet were not evaluated in this work. No evaluation as to the difficulty for other potential PM titanium sheet producers to attain the level of compentance shown by Ametek was performed.

In this work a vacuum or inert gas sintering furnace was an identified piece of equipment that is commercailly available but has not been applied to the task of binder removal / sintering of titanium roll compacted sheet. Such a furnace would ideally be colocated adjacent to roll compaction due to the fraility of the roll compated sheet. Ametek would be a logical choice for the location of the vacuum inert gas furnace should an integrated manufacturing facility be viable.

Several barriers exist for PM-Ti sheet. Low cost sheet is not yet attainble due to economis of scale and lack of complete facility integration. When this work was conceived in the latter part of CY 2008 the market conditions were trending toward high prices and long deliveries for Kroll processed titanium sheet. Titanium sheet produced via the Kroll process is readily available today, for an acceptable price and delivery, retarding industrial interest in PM-titanium.

5. ACCOMPLISHMENTS

The project demonstrated that titanium sheet from powder could be produced via roll compaction and thermomechanical deformation by three different processing routes. Sheet was produced from HDH titanium powder following one of the processing routes using a multi-company commercial infrastructure. The sheet was tested for mechanical performance and installed in a protoype heat exchanger for a short duration test and was found to adequately exchange heat.

6. CONCLUSION – RECCOMENDATIONS

Formability of PM-Ti sheet produced from HDH reduced titanium remains below that of aerospace grade titanium produced via the Kroll process. Even though formability is not a specified test to meet the standards, it is an expectation that when the ASTM B-265 properties are met, that formability can be predicted based on 50 plus years of prior experience with titanium. PM-Ti does not follow that predictability hence specifications specific to PM-Ti is a recommended future effort. An industrial supply chain to convert HDH based titanium powder exists within the current industrial infrastructure and can produce an industrial grade of titanium sheet with no new capital investment. The industrial grade PM-Ti sheet thus produced was found to perform in short duration saltwater heat exchanger tests; long duration testing for that application is recommended.

7. REFERENCES

[1]US Patent 2,205,854, Method for Manufacturing Titanium and Alloys Thereof, W. Kroll, June 25, 1940.
[2]Rivard, J.D.K. et al. JOM 57, 11, 2005. pp. 56-60
[3]Kraft, Ed. Department of Energy Internal Report: Industrial Markets for Titanium
[4]American Society for Testing and Materials ASTM B-265-11
[5]Peter W.H et al JOM Vol. 64, No.5, 2012 pp. 566-571
[6]Cantin, G. M. D. et al. Powder Metallurgy, 54, 3, 2011, 188-192.
[7]Stone N. et al. Materials Science Forum Vols. 618-619. 2009. Pp. 139-142
[8]J. Beal, R. Boyer and D. Sanders, Forming of Titanium and Titanium Alloys, Metalworking: Sheet Forming, Vol 14B, ASM Handbook, ASM International, 2006, p 656–669
[9]WHO/UNICEF Joint Monitoring Programme (JMP) for Water Supply and Sanitation. (2010). Progress on Sanitation and Drinking-Water, 2010 Update.
[10] Donachie, M.J. Jr, Titanium: A Technical Guide 2nd Edition, ASM International 2000, pp 85-87
[11] Website http://web.mit.edu/seawater/ Thermophysical properties of seawater
[12] Website http://www.pure-aqua.com/osmotic-pressure-calculator.html
[13] Website http://www.timet.com/images/document/sheet/TIMETAL_35A.pdf

8. PUBLICATIONS, PRESENTATIONS, PATENTS

A portion of the work content here was a significant portion of the writings in reference 5 above. Journal of Metals, Volume 64, number 5, July 2012 pages 566-571. A portion of the work was presented at The Powder Metallurgy Conference held in Hollywood Florida, in 2010, an expansion of that was presented at the International Titanium Association (ITA) Conference in Kissimmee, Florida in 2011, and additional information at the ITA in San Diego, CA in 2012. No patents have been applied for in regards to this work.

Appendix A

AQUA-CHEM EXPERIENCE VERSUS ASTMB265 SPECIFICATION

Appendix A. AQUA-CHEM EXPERIENCE VERSUS ASTMB265 SPECIFICATION

The challenge communicated by Aqua-Chem is revealed in a discussion about the specification of material and the practicalities of production. Aqua-Chem produces custom heat exchangers that provide a profitable competitive advantage to the markets they serve. The heat exchangers of interest for this work were plate heat exchangers with a proprietary herringbone dimple pattern. For production economy, tooling used in the forming press to create the herringbone /dimple pattern on the metal sheets is designed to accommodate either duplex stainless steel, or titanium without a tool change. The use of the tool on multiple materials allows for cost advantages, avoiding a press shut down for a tool change, and also avoiding the need for two tool sets that can cost a significant sum. For the press tool to work on either titanium or stainless steel, the two materials have to have comparable and predictable forming characteristics. Usually the press tooling is an evolutionary design that evolves based on some trial and error with shape control adjustments being made to the tool based on dimensions of the formed part produced by the tool. The shape adjustments to the tool are made with the confidence that materials used to qualify the tool are bounded by a material property specification. For titanium and Aqua-Chem's need, ASTM B265 Grade 1is specified. Production trials have shown that even though grade 1 is not needed for service, it is needed to maintain the single-tool-in-the-press-criteria. Formability is not a specified test parameter in the ASTM specifications; however Aqua-Chem has found that if ASTM B265 Grade 1 is purchased then the result are favorable.

Timet, a titanium sheet metal producer has supplied TIMETAL 35A[13] to Aqua-Chem to meet the ASTM B265 Grade 1 Specification. TIMETL 35A has a UTS minimum of 50 ksi, a minimum yield strength of 31.9 ksi and an elongation of 35%; clearly superior to the minimum 24% elongation called out in ASTM B265 for Grade 1 , and certainly qualifying for sale as ASTM B265 Grade1 metal. When Aqua-Chem, who specified ASTM B265 Grade 1, successfully forms and stamps TIMETAL 35A into the design shape both customer and supplier are content. The customer expectation is now in place whereby specifying ASTM B265 Grade1 results in success. However, if material complying with ASTM B265 Grade 1 minimums, where the elongation is 24% it may not meet the customer's expectation. In this work Aqua Chem communicated just such an event. In that foreign produced lower cost ASTM B265 Grade 1 titanium could not be formed into the desired shape using the standard practice, and the foreign source was deemed poor quality and unacceptable, even though it met the ASTM specifications.

The situation manifests itself in the powder metallurgy sheet produced in this work. Materials meeting the ASTM B265 specification do not meet the expected customer criteria for similar grades based on the evolution of the modern Kroll process and the quality improvements in produced metal over the 50 plus years of titanium's commercial existence, that are not reflected in the specification.

The current state of the powder metallurgy produced sheet in this study is that even though it meets ASTM B265 specifications it does not meet equivalency with wrought material based on formability trials.