K. Low-Cost Titanium Powder for Feedstock

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Objectives

- Investigate alternate powder and melt-processing methods for low-cost titanium materials.
- Evaluate processing methods to produce powder metallurgy (P/M) titanium products with International Titanium Powder, Inc. (ITP) powder.
- Evaluate the suitability of emerging titanium technologies for the production of low-cost titanium products for automotive applications.

Approach

- Perform characterization and analysis of the sintering behavior of the ITP powder. Provide feedback of results to ITP for use in process design.
- Develop low-cost feedstocks for P/M use in automotive applications from low-cost titanium chloride ($TiCL4$)
- Perform thin-section slab castings and roll to sheet to simulate and evaluate the use of continuous-casting methods to produce sheet materials.
- Survey the emerging technologies for the low-cost production of titanium powders and evaluate for use in automotive applications.

Accomplishments

- Developed press-and-sinter cycles that produced greater than 97% dense plates of cold-pressed (CP) titanium from the ITP powder. Tensile tests from the plates exhibited no measurable ductility.

- Plates pressed and sintered from CP titanium ITP powder hot rolled with a 2.5:1 reduction, exhibited limited ductility in tensile tests. Fracture surface evaluation showed that, although densities were high, large amounts of the powder had not sintered.
- Designed and fabricated in cooperation with Albany Research Center and CANMET, graphite molds for plate casting trials to determine the effect of solidification rate on the reduction of area required to produce wrought properties. Castings 1/8, ¼ and ½ inch in thickness were prepared.
- Evaluated step-plate castings for mechanical properties which indicated that castings made in permanent molds without hot isostatic pressing (HIP) can exhibit adequate mechanical properties.

Future Direction

- Perform dilatometry, thermogravimetric (TGA), microstructural analysis and x-ray diffraction (XRD) analysis to develop a sintering cycle that can eliminate Na impurities and improve sinterability at lower pressing pressures.
- Continue the development of sintering cycles for the ITP powder with an emphasis on understanding the sintering mechanisms of the powder to increase ductility.
- Evaluate alternate low-cost titanium feedstocks for powder or melt processing to wrought products.

Introduction

An automobile design trend that has received much attention has been the reduction of vehicle mass. Reducing mass can improve both performance and fuel economy. While design changes can play a large role in reducing mass, large reductions ultimately will require the substitution of higher specific strength/stiffness materials in place of carbon steel. Primary contenders in this race are high-strength steels, aluminum, and fiber-reinforced polymer composites. One material, not on this short list, but one that could provide further reductions, is titanium. Although titanium is light and strong, its role in the automobile has been almost nonexistent because of its exorbitant price. This high price is a direct result of the current production route, the Kroll process, which is time-consuming; energy-, capital-, and labor-intensive; and batch-based.

However, new technologies are emerging that may change the characteristics of the titanium market. In particular, these technologies may reduce the titanium price sufficiently to allow it to compete in high-volume markets, possibly even automotive. This project examines the powder metallurgy (P/M) behavior of titanium powder produced by a new process being developed by ITP.

Approach

The production of low-cost titanium for automotive applications will require cost reductions in both raw materials and secondary processing operations. The approach to this project will be to evaluate the suitability of emerging titanium beneficial technologies for the production of low-cost automotive components. The ITP powder process produces an alloy powder with morphology very similar to other emerging technologies, Fray-Farthing-Chen (FFC) Cambridge and MER anodic reduction. Because ITP can produce powders in sufficient quantity for evaluation, the ITP process will be used as the basis for the evaluation.

Results and Discussion

Previous reports (1, 2, 3) of ITP powder processing indicated that sodium compounds were assumed to be limiting the density and tensile ductility of the sintered pressing. Thermo-gravimetric (TGA) results of ITP powders indicated that sodium compounds were present and began to decompose at temperatures near 500°C. Using previously reported 1150°C sintering cycles (4) plates were pressed, consolidated and tested for mechanical properties using a standard ASTM E8 tensile sample tested at 12 mm/mm/minute strain rate. The tensile tests exhibited little or no ductility in the as-sintered condition. The failure strength of the as-sintered sample was 510 MPa and occurred slightly after yield of the sample. The measured strain in the as-sintered sample was less than was less than 0.07%. The samples that were as-sintered and rolled exhibited yield and ultimate strengths of 560 and 570 MPa, respectively with an elongation of 4%.

A sample 12-mm-diameter by 12-mm-long was vacuum hot-pressed at 750°C using the hot press at Wright Paterson Air Force Material Laboratory. From the vacuum hot-pressed bar, sub-scale tensile samples were machined and tested at a constant crosshead speed of 12 mm/mm/minute. The vacuum hot-pressed sample exhibited 100% density, yield and ultimate tensile strengths of 525 MPa and 570 MPa, respectively and an elongation of 17%. Tensile test results for the powder processed materials are given in Table 1.

Analysis of the fracture surface of the pressed, sintered and rolled tensile sample indicates that relatively complete consolidation of the powder has been achieved, as shown here by Figure 1.

The low-cost, ilmenite-based $TiCl_4$ and standard grade of $TiCl_4$ provided by DuPont had the compositions given in Table 2. The low-cost $TiCl_4$ exhibited elevated Sn and Si concentrations of 406 and 55 ppm, respectively, compared to standard $TiCl_4$ where Sn and Si are less than 50 and 10 ppm,

Table 1. Tensile properties measured from parts processed from ITP powder using various consolidation methods. Typical properties for ASTM CP TI Grade 3 have been included for comparison.

	Yield Strength	Ultimate Strength	Elongation
Processing Conditions	MPa	MPa	%
Pressed and Sintered	N/A	510	<0.07
Pressed, sintered and rolled	560	570	4
Vacuum Hot Pressed at 750°C	525	590	17
Grade 3 CP Ti, Typical	455	560	20

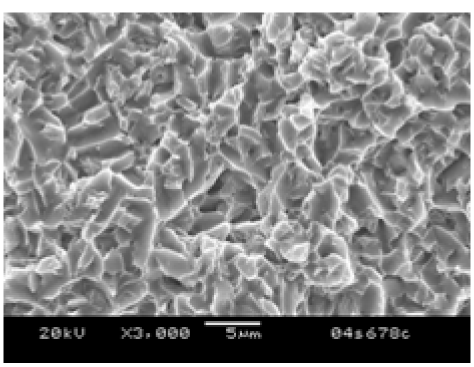


Figure 1. Fracture surface of sintered compacts of ITP powder indicating that relatively complete sintering of the compact has been achieved.

Table 2. Comparison of chemical composition of standard and low-cost, ilmenite based $TiCl_4$.

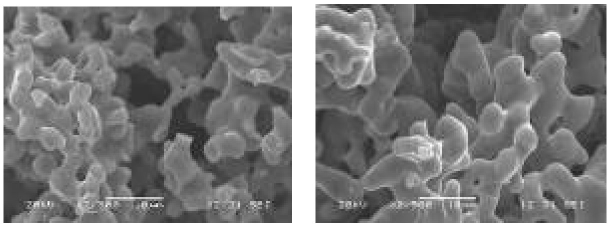
Element	Standard $TiCl_4$	Low-Cost, Ilmenite-Based $TiCl_4$
	ppm	ppm
Sn	50.00	408.3
Si	10.00	55.4
Mg	10	8.6
Ca	10	4.6
V	3.00	3.9
Cu	1	3.7
Sb	5.00	3.3
Zn	5	2.9
Fe	1.00	1.9
Al	2	1.5
Pb	5	1.5
As	2.00	1.4
Cd	N/A	1.4
Mn	1	1.4
Ni	25	1.4
Nb	N/A	1.4
Zr	10	1.4
Ba	1.4	1.4
Cr	1	0.7
Co	1.4	tr
Hg	<0.35	<0.35

respectively. The ilmenite-based $TiCL_4$ produced by DuPont had less than 2 ppm Fe as a result of a distillation process used to produce FeCl for sale to the chemical industry (resulting in reduced $TiCl_4$ cost).

The low-cost, ilmenite-based $TiCl_4$ feedstock received at ITP has been processed to powder using the "Engineering Loop." No processing problems were encountered with low-cost $TiCl_4$. Figure 2 is a micrograph of the ITP standard and low-cost $TiCL_4$ powder. No obvious difference in powder morphology was observed when comparing the standard and ilmenite based $TiCl_4$ ITP powders, shown in Figure 2.

The powders produced by ITP exhibited an open-pore structure shown in Figure 3 and, as a result, have a relatively low tapped density of approximately 7%. Although a tapped density of 7% is workable for many P/M applications, ideally the tapped density will be higher.

As a result, milling trials were initiated at PNNL to break down the powder and develop a higher tapped density. Ideally, the powder would fracture at the



(a) (b)

Figure 2. ITP powder produced with low-cost, ilmenite-based $TiCl_4$ (a) and standard $TiCl_4$ (b) indicating little change in powder morphology. Note the ligament type structure in the as-received powders.

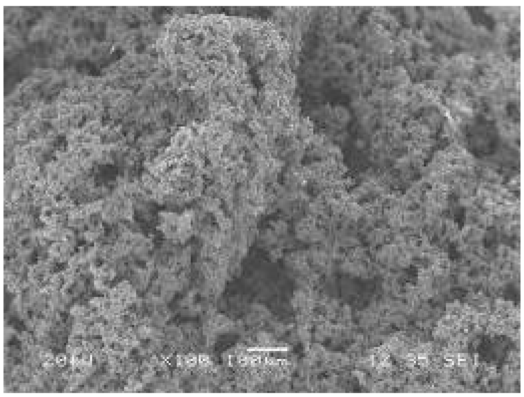


Figure 3. Typical as-received ITP powder that exhibits a tapped density of approximately 7% of theoretical.

ligaments shown by Figure 2 and produce a fine sub-micron powder size; however, the ITP powder is very ductile-cold-welded readily into agglomerates as shown by figure 4. The finest powder sizes achieved are represented by Figure 5 and resulted in tapped densities in excess of 35%.

All Ti6Al4V step-cast plates were completed and delivered to CANMET for evaluation. Figure 6 has been included to illustrate the typical step-cast plate developed by AlRC and PNNL and delivered to CANMET. Each step of the casting was evaluated for tensile properties using sub-size (4 mm) ASTM E8 tensile samples.

The ultimate strength for the plates increased from 928 to 984 MPa as the section thicknesses decreased from 25 to 3.2 mm. No discernable differences in yield strength and elongation were observed with section thickness. Table 3 has been included and summarizes the tensile results reported by CANMET[5].

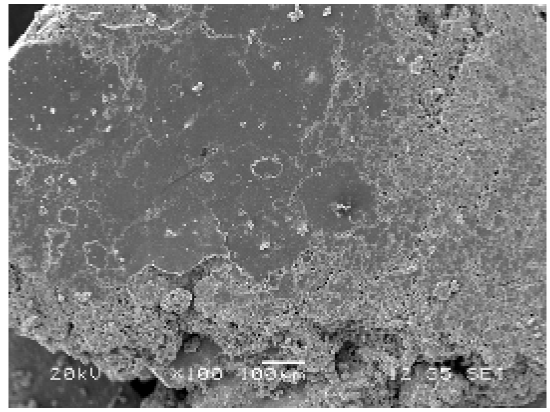
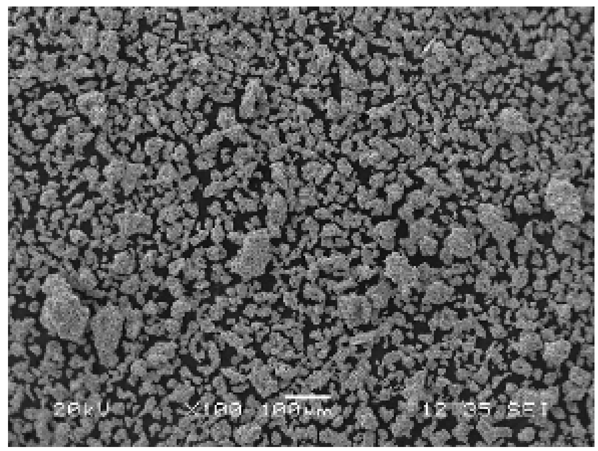
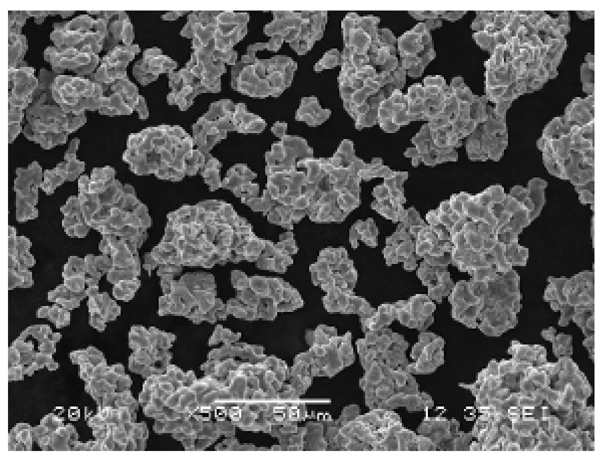


Figure 4. Cold-welded agglomerates due to over-milling of the very ductile ITP powder.



(a)



(b)

Figure 5. Milled ITP powder that exhibits tapped density in excess of 35% at 100x (a) and 500x (b).

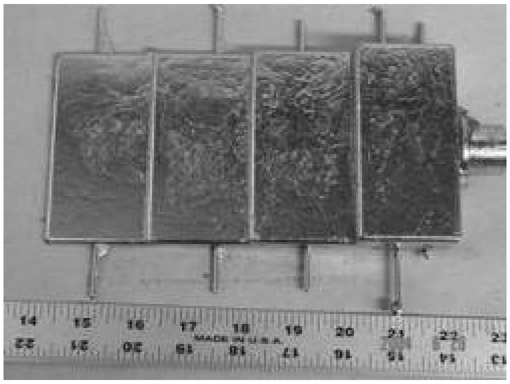
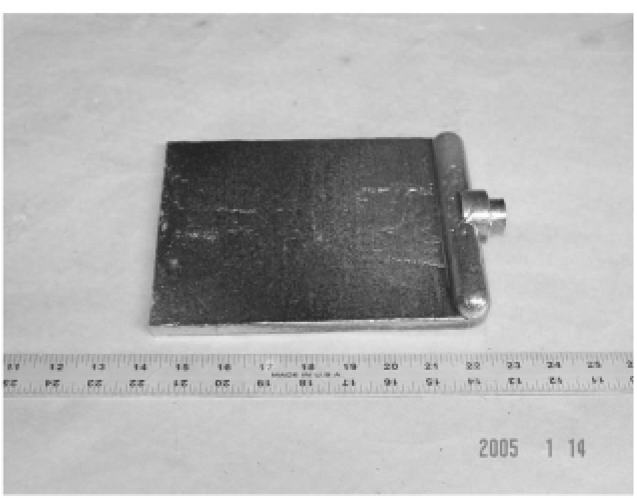


Figure 6. Step-plate castings developed for evaluation at CANMET.

Table 3. Tensile properties measured by CANMET from the step-plate castings produced by AlRC.

Section Thickness	0.2% Offset Yield Strength	Ultimate Strength	Elongation
Mm	MPa	MPa	%
25	823	928	7
13	836	951	7
6.3	817	958	9
3.2	824	984	6
Ti6A14V – Cast and HIPed	870	960	10

Ti6Al4V cast plates have been prepared at AlRC for additional characterization for tensile and fatigue strength developed by low levels of hot rolling. Characterization of the plates prior to hot rolling has been initiated. An example of the plates to be used for evaluation of solidification rate and property relationships has been included in Figure 7.



Ti-6-4 plate 0.5P2, side 2

Figure 7. Monolithic cast plate to be used for hot rolling and Solidification-rate analysis.

Conclusions

- As indicated by the strength and ductility levels produced in the vacuum hot-pressed samples, the powder produced by ITP can develop near wrought-like properties in CP Ti.
- Sintering conditions for the ITP can be developed to produce ductility. Optimization of the sintering cycle must be performed to maximize ductility.
- The low-cost, ilmenite-based $TiCl_4$ -produced powder is visually very similar to the standard $TiCl_4$ powders.
- The impurities observed in the low-cost ilmenite-based $TiCl_4$ are Sn and Si after FeCl removal by distillation.
- The sintering mechanism of the ITP powder is different than atomized powder and conditions must be developed to maximize the volume of powder sintered.
- Thin-plate castings of Ti6Al4V can produce properties near that of cast and HIPed casting using a simulated permanent mold made from graphite.

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