M. Low-Cost Titanium Powder for Feedstock

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Objectives

- Investigate alternate powder and melt processing methods for low-cost titanium (Ti) materials.
- Evaluate processing methods to produce powder metallurgy (P/M) Ti products with International Titanium Powder, Inc. (ITP) powder.
- Evaluate the suitability of emerging Ti technologies for the production of low-cost Ti 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 Ti tetrachloride ($TiCl_4$).
- 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 Ti powders and evaluate for use in automotive applications.

Accomplishments

- Observed decreased swelling in low-cost-$TiCl_4$-produced powders and attributed the improvement to the increase in the onset of sintering temperature that allows Na-bearing compounds to decompose.
- Developed press-and-sinter cycles that produced greater than 97% dense plates of cold-pressed (CP) Ti from the ITP powder.

- Developed sintering cycles that produced 95+% dense bars of CP Ti that exhibit ductility of up to 14% in selected samples from standard tensile tests using low-cost $TiCl_4$.
- Produced and characterized CP Ti powder produced by ITP and DuPont from two impurity levels of $TiCl_4$. The major powder characteristics showed no differences.
- Tensile-test samples produced from the low-cost $TiCl_4$ had very similar behavior to the higher-purity samples indicating that the low-cost $TiCl_4$ is a viable low-cost feedstock stream. The tensile characteristics of the sintered samples are strong functions of the oxygen equivalent for the powder and this was not affected by the $TiCl_4$ purity.
- Using a commercial P/M die, pressed approximately 100 gears to learn practical issues associated with the new Ti powders.

Future Direction

- Perform dilatometry, thermogravimetric analysis (TGA), microstructural analysis and x-ray diffraction (XRD) analysis to develop a sintering cycle that can eliminate Na impurities and improve sinterability.
- Investigate milling and compaction methods to reduce the high O and N content and/or fine powders.
- Continue the development of sintering cycles for the ITP powder with an emphasis on understanding the sintering mechanisms of the powder to increase ductility.
- Investigate in-die lubrication options for high-volume Ti die pressing.
- Evaluate alternate low-cost Ti 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 Ti. Although Ti 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 Kroll production route which is time-consuming; energy-, capital- and labor-intensive; and batch-based.

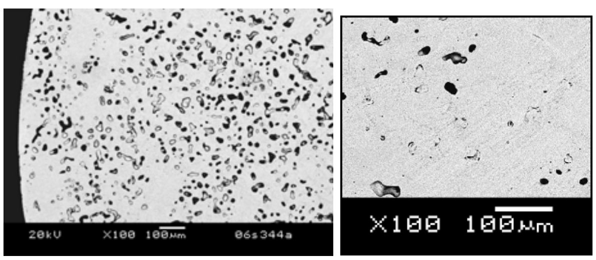
However, new technologies are emerging that may change the characteristics of the Ti market. In particular, these technologies may reduce the Ti price sufficiently to allow it to compete in high-volume markets, possibly even automotive. This project examines the P/M behavior of Ti powder produced by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

Approach

The production of low-cost Ti 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 Ti 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 such as 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 Na compounds were assumed to be limiting the density and tensile ductility of the sintered pressing. TGA results of ITP powders indicated that Na 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 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%. By decreasing the sintering time and increasing the temperature, better densification has been achieved allowing more rapid sintering to occur prior to the onset of swelling associated with Na-compound decomposition. Samples sintered at 1250°C for 20 minutes exhibit densities of 97+% of theoretical density and samples sintered for 8 hours had densities of 90%. With extreme sintering conditions, the swelling can reduce the density to below the starting density; an example is given in Figure 1a and compared to dense region of Figure 1b.



(a) (b)

Figure 1. Sintered microstructures showing severe swelling with 8 hour 1250°C sintering (a) and a relatively dense region (b).

Ductility of up to 14% in machined tensile samples at strength levels of 450 to 500 Mpa has now been achieved. Table 1 has been included to show tensile strengths and ductilities observed with the new sintering conditions. The ITP powders made from low-cost $TiCl_4$ have exhibited slightly higher as-sintered densities, in all cases, when compared to the standard process. This is likely to be explained by the effect of trace impurities on the onset of sintering. The low-purity $TiCl_4$ ITP powder showed no swelling in dilatometer testing and the onset of sintering was increased from 400°C to 900°C, as shown in Figure 2. The significance of the temperature increase is related to the decomposition of Na-bearing compounds, where most known Na compounds decompose above 400°C and less than 900°C.

Table 1. Tensile properties for low and high purity $TiCl_4$ powders produce by ITP (R1 U2.2 and ITP-LP) and DuPont (D11001 and 500414).

			Strength		
Lot	TiCl4 Purity	Theoretical Density, %	Yield MPa	Ultimate MPa	Elongation %
500414	High	92	413	553	14
D11001	Low	92	455	581	8
R1 U2.2	High	87	434	476	4
ITP - LP	Low	92	602	686	6

The standard allowable elements for high grade $TiCl_4$ are given in Table 2. The low-cost $TiCl_4$ exhibited elevated concentrations of trace elements compared to standard $TiCl_4$ and were less than 2000 ppm in the final metal powder. The ilmenite-based $TiCl_4$, produced by DuPont, had less than 2 ppm Fe because of a distillation process used to produce FeCl for sale to the chemical industry (resulting in reduced $TiCl_4$ cost).

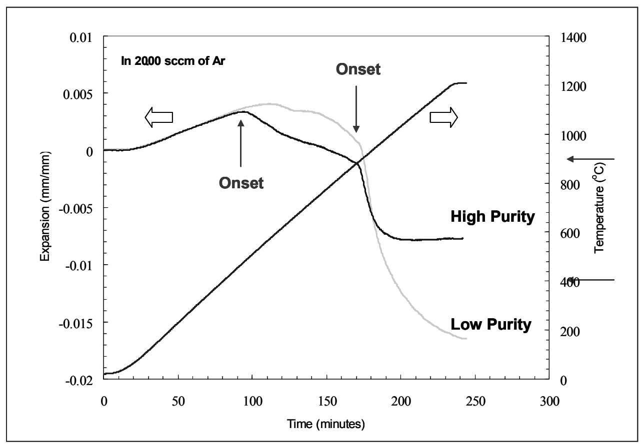
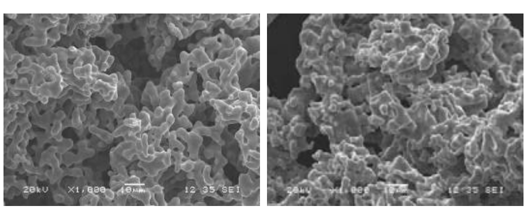


Figure 2. Dilatometer curves for the low-purity and high-purity $TiCl_4$ ITP powders. The presence of trace impurities have altered the onset of sintering and have increased the sinter-start temperature from 400°C to 900°C. The increase from 400°C to 900°C is significant to the decomposition of Na-bearing compounds.

The low-cost ilmenite-based $TiCl_4$ feedstock was received at ITP and DuPont and has been processed to powder using the each supplier's respective process. No processing problems were encountered with low-cost $TiCl_4$ and each supplier noticed little handling differences. Figure 3 is a micrograph of the ITP and DuPont powders showing typical morphology and structure found in Na-reduced $TiCl_4$. Powders processed using standard and low-cost $TiCl_4$ powders exhibited no obvious difference in powder morphology for both ITP and DuPont as shown in Figures 4 and 5, respectively.

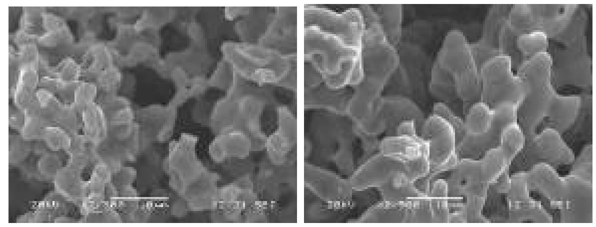
Table 2. Comparison of chemical composition of standard and low-cost-ilmenite-based $TiCl_4$.

Element	Standard $TiCl_4$
	ppm
Sn	50.00
Si	10.00
Mg	10
Ca	10
V	3.00
Cu	1
Sb	5.00
Zn	5
Fe	1.00
Al	2
Pb	5
As	2.00
Cd	N/A
Mn	1
Ni	25
Nb	N/A
Zr	10
Ba	1.4
Cr	1
Co	1.4
Hg	<0.35



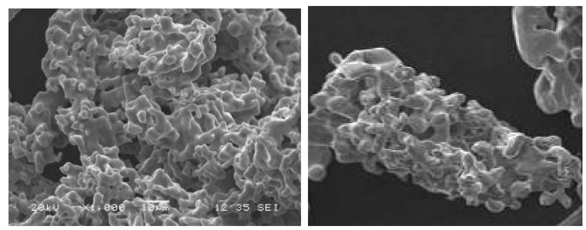
(a) (b)

Figure 3. Powders produced by ITP (a) and DuPont (b) from low-cost ilmenite-based $TiCl_4$ showing morphology typical for Na-reduced powders and very similar structure for the two suppliers.



(a) (b)

Figure 4. 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.



(a) (b)

Figure 5. DuPont powder produced with high-purity $TiCl_4$ (a) and low-cost $TiCl_4$ (b) indicating little change in powder morphology.

The particle-size analysis of the as-received powders indicated that DuPont and ITP processes produce a different distribution; however, the low-cost $TiCl_4$ did not affect particle distribution. Figure 6 is a histogram showing powder-size distribution for the ITP and DuPont powders made from low- and high-purity $TiCl_4$.

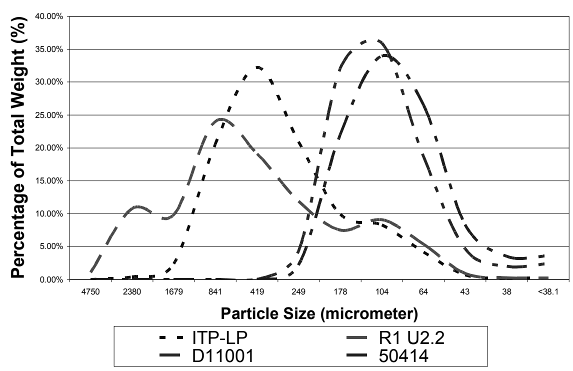


Figure 6. Particle-size distribution for low-cost $TiCl_4$ DuPont and ITP (50414 and ITP LP, respectively) and standard (D11001 and R1 U2.2, respectively) $TiCl_4$ powders. The distribution indicates a difference for each supplier but no difference for $TiCl_4$ purity.

The ITP powder and DuPont powders had different trace element levels, which were attributed to slight differences in the $TiCl_4$ used at both suppliers. Summary of the typical impurities found in the powders are in Table 3. O content for the powders was found to range between 1780 and 2400 ppm and was lowest (1780) in the low-purity ITP powder and highest (2400) in the high-purity ITP powder. The DuPont low- and high-purity $TiCl_4$ powders were 2100 and 1890 ppm O, respectively. Although the differences in O appear slight, the content variation is enough to alter the mechanical properties substantially. The primary differences in the powders were the N, Na and Cl contents. The low- and high-purity ITP powders had 50 and 80 ppm, respectively, and the DuPont powder was below the detectability limit of 20 ppm (lower limit N test are being performed). N is an interstitial element and behaves similar to O in Ti. The Na content for the ITP and DuPont powders were 330 and 110 and 1300 and 1200 ppm for the low- and high-purity $TiCl_4$, respectively. Cl was 1100 and 1400 and 19 and 21 for the low- and high-purity $TiCl_4$ DuPont and ITP powders, respectively. The form of Na and Cl in the ITP powder is unclear and could not be found in SEM analysis of metallographically-prepared samples or fractured surfaces using EDS and WDS analyses, indicating that it may be in the powder solid solution; however, NaCl particles were found on the fracture surfaces of the DuPont tensile samples and would be expected to reduce mechanical properties. Figure 7 shows an example of a Na- and Cl-rich particle found on the fracture surface of a DuPont-powder tensile sample.

Table 3. Comparison of metal powder chemistry for ITP (HP and LP) and DuPont (D11001 and 500414) low-cost $TiCl_4$ (ITP-LP and D11001) and standard $TiCl_4$ (ITP-HP and 500414).

	ITP-HP	**ITP-LP**	**D11001**	**500414**
Element	ppm	ppm	ppm	ppm
C	93	55	74	105
Cl	19	21	1100	1400
N	77	47	<20	<20
Na	330	110	0.13%	0.12%
O	2400	1780	2100	1890
O-equiv	2554	1874	2100	1890
BET (m^2/g)	0.31	0.31	0.30	0.45

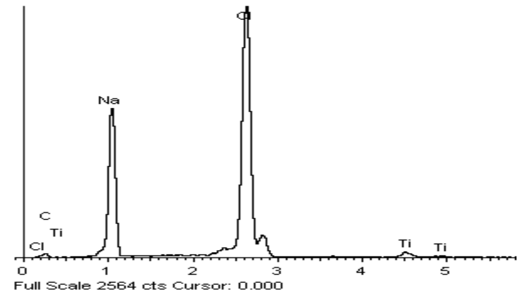
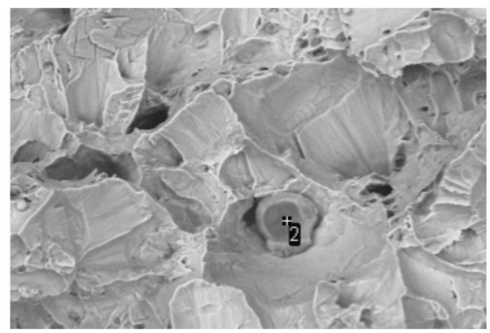
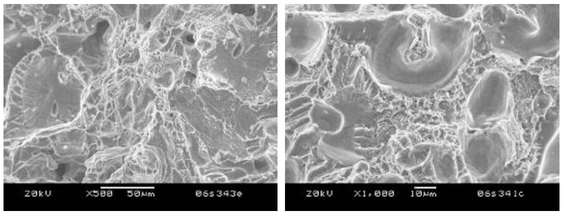


Figure 7. Na- and Cl-rich particle, noted as 2, in SEM fracture surface (below) and corresponding EDS analysis (above).



The trace elements found in the $TiCl_4$ and in the powder were not found at fracture surfaces or in particulates within the structure, indicating that, as predicted from the binary phase diagrams, all of the impurities are in solid solution. This favorable result indicates that no gross intermetallics were formed and that the trace elements are not expected to impact properties such as fatigue or ductility. A solid-solution strengthening effect may be found, however, given the elevated O and N contents of the powders; the low levels of trace elements may be difficult to discern. Fracture-surface analysis shown in Figure 8a and b for ITP and DuPont powders, respectively, showed no preferred initiation site and exhibited a mix of ductile rupture, cleavage and porosity.

The high strength and corresponding low ductility of the tensile samples continues to be problematic. A simplified oxygen-equivalent equation (O+2N) was applied to the four powder types. The oxygen equivalent shows that all strength variation within the samples can be attributed to the O and N content, as shown by the linear correlation in Figure 9, with oxygen equivalent and 0.2% offset yield. This is a favorable result with respect to the low-cost $TiCl_4$ in



(a) (b)

Figure 8. Fracture surface of sintered compacts of ITP (a) and DuPont (b) indicating a mixed failure mode of ductile rupture and cleavage. No trace elements were found on the fracture surfaces indicating that the low-cost TiCl4 had not adversely affected ductility.

that trace elements are having a minimal effect on the properties; however, the O and N content must be better controlled.

In pressed and sintered samples, the O content is elevated by approximately 1200 ppm. The source of the increase is each prior process step (milling (700ppm), pressing (200ppm) and sintering (300ppm)) and must be controlled in a different manner than currently used. The initial step will be to screen out fines (less than 400 mesh) that have O contents in excess of 4000 ppm. To date, milling has been done using a Spex mill and has produced nearly 25 weight percent fines containing 4000 ppm O (milling is done in an Ar-filled glove box, however, the powders must be passivated in air for safe handling). Therefore, a milling process will be employed to reduce the generation of fines.

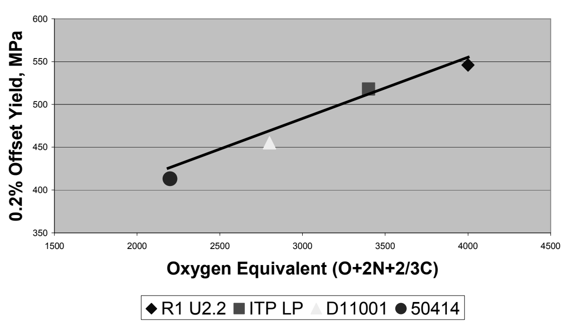


Figure 9. Correlation of yield strength and oxygen equivalent for low-cost $TiCl_4$ DuPont and ITP, 50414 and ITP LP, respectively, and standard $TiCl_4$ powders D11001 and R1 U2.2 for DuPont and ITP, respectively.

Powders milled at PNNL were pressed using a high-rate commercial P/M die located at Western Sintering, LLC, Richland, WA. The die used was a gear developed for commercial production of a helicopter rotor-balancing assembly that has been discontinued. A green pressing of the gear from low-cost-$TiCl_4$ ITP powder can be found in Figure 10. The trials provided insight into the characteristics needed for the use of Ti powder in commercial Ti applications. The trials were performed using a hydraulic press operated at an equivalent rate of 45 parts per minute at pressing pressures of 80,000 pounds per square inch (40 tons per square inch). The initial trails were performed without lubrication due to Ti's reactive nature and the potential for the very high green strength part being more robust; however, within 10 pressings, cracking was observed in the pressed part. The cracking was attributed to galling in the die resulting in tensile stresses during part ejection. The die was cleaned and a series of pressings were made using lithium stearate die lube with very little improvement. Additionally, the fines were left in the powder blend and caused interference with the punch and die. Therefore, a second series of trails were performed using powders blended with various lubricants used in commercial powder-metal production which resulted in no improvement. For the trials it was learned that 1) the ITP powder must be milled to produce a low fraction of fines and a separation step must be added and 2) in-die lubrication will be required to minimize reaction with the Ti and provide an adequate barrier to prevent galling.

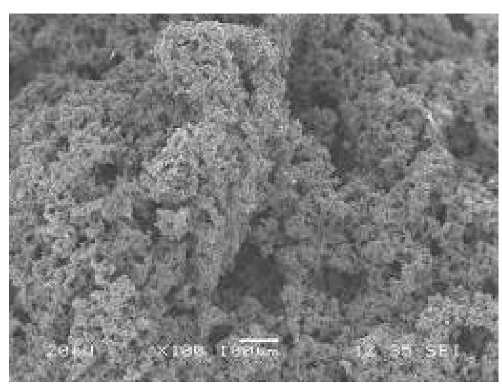


Figure 10. Typical as-received ITP powder that exhibits a tapped density of approximately 8% of theoretical.

Lubrication is commonly used in P/M; however, lubrication is more complicated in Ti due to the reactivity. In Fe-based P/M, lubricants are added directly to the powder and are either removed during a pre-heat portion of the sintering cycle or used to react with the powder and form wear-resistant carbides. In extreme cases of die complexity, in-die lubricants are used with Fe-based P/M to facilitate part compaction or ejection. However, Ti will react readily with common powder and die lubricants and die materials such as Fe-based steels and the binder of carbide(W, Hf etc…)-cemented carbide tools. In order to evaluate the suitability and effectiveness of powder and die lubes, an instrumented die has been constructed that will enable direct measurement of friction factor and compaction and ejection force. See Figure 12.

The powders produced by ITP exhibited an open pore structure, shown in Figure 11, and, as a result, have a relatively low tapped density of approximately 8%. Although a tapped density of 8% 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. The trial indicated that ITP powder, although very ductile, was readily milled and that tapped densities could be increased to in excess of 45%. As mentioned previously, the fraction of powder less than 400 mesh is 25 weight-percent and contains more 4000-ppm O and 290-ppm N using the current milling practice. This practice will be re-evaluated, and a balance between O content and apparent and tapped densities will be established. Initial milling trials using less-aggressive media have improved tapped density and powder morphology, as shown in Figure 13, where the open pore structure shown by figure 10 has been compacted into a more globular network, without fracture, into smaller particles. In limited trials, the milling process development is ongoing and has shown improvement in both green and as-sintered densities.

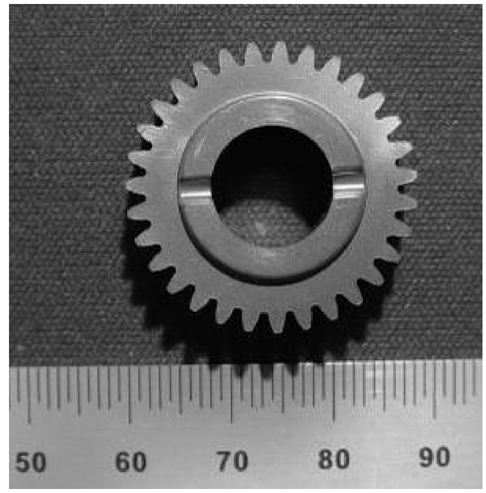


Figure 11. Commercial die-pressing using low-cost $TiCl_4$ ITP powder.

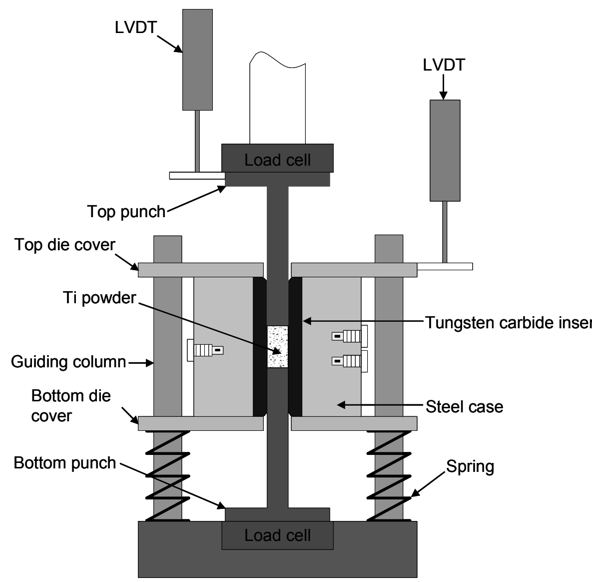


Figure 12. Instrumented die to be used for lubrication development.

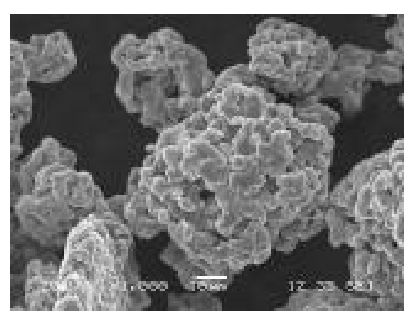


Figure 13. Alteration of ligament structure (compared to Figure 10) for ITP milled using less-aggressive parameters.

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 processed powders have been developed to produce ductility of 10% in selected samples, with average values at approximately 8%.

The added trace elements have not affected the tensile properties of samples machines from sintered bars. The largest effects on mechanical properties are from O and N.

Optimization of the sintering cycle must be performed to maximize ductility, and will be focused on the elimination of Na-induced swelling.

The morphology, surface area, and particle-size distribution of the low-cost ilmenite-based $TiCl_4$ was very similar to the standard $TiCl_4$ powders.

Powder milling, compaction, and sintering methods will be evaluated for O and N reduction. Commercial die pressing will require that the powders are milled to reduce the fraction of fines.

Commercial die pressing will require the use of an in-die lube system to form a barrier between the die steel and Ti powder.

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