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# Letter Effects of TiCl<sub>4</sub> purity on the sinterability of Armstrong-processed Ti powder K.S. Weil\*, Y. Hovanski, C.A. Lavender

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### 1. Introduction

Most titanium commercially produced today is synthesized via the Kroll batch process, in which purified titanium tetrachloride (TiCl<sub>4</sub>) is chemically reduced with molten magnesium to form metal sponge [1]. This largely replaced an earlier method of titanium production, known as the Hunter process, that employs liquid sodium as the reductant [2]. An advancement in titanium production at the time, the Kroll process consists of a series of batch steps, a number of which remain labor intensive, inefficient, and expensive [3]. As a result, a number of process improvements and alternative production approaches have been subsequently considered [4.5]. One of these is a low-cost alternative known as the Armstrong process, currently under development at International Titanium Products, LLC (ITP). Utilizing the same chemistry as the Hunter process, the Armstrong process produces titanium powder via the reduction of TiCl<sub>4</sub> vapor injected into a molten sodium stream [6]. Since the rate of sodium flow exceeds that required for stoichiometric reaction with the incoming TiCl<sub>4</sub>, the excess cools the reaction products and transports them to a separation vessel where both the sodium and the salt byproduct are removed. The process yields a continuous stream of commercially pure titanium (cp-Ti) powder and through modification, can also directly produce alloy powders such as Ti-6Al, 4V. Independent economic studies prepared for the U.S. Department of Energy and the U.S. Defense Advanced Research Project Agency [7,8] indicate that the cost of

### ABSTRACT

The sintering behavior of titanium powder produced via the Armstrong process from two different grades of  $TiCl_4$  was investigated by a combination of thermal, chemical, and microstructural analysis techniques. It was found that the use of lower grade  $TiCl_4$  leads to higher part density due to a difference in sintering behavior that affects the entrapment of volatiles within the sintered body.

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producing titanium by this process is proportional to the costs of the reactants; i.e. the use of low-cost TiCl<sub>4</sub> will substantially reduce the cost of Armstrong-produced titanium powder.

TiCl<sub>4</sub> is typically produced by chlorination of titanium-bearing minerals such as high-grade ilmentite and rutile [9]. Conversion takes place in a fluidized bed reactor at 850–950 °C using petroleum coke as a reductant and forms volatile metal chlorides that are collected and separated by fractional condensation, double distillation, and chemical treatment [10]. Iron chloride (typically FeCl<sub>3</sub>) is the chief byproduct of fractional condensation and is sold as an industrial commodity. Additional trace metal chlorides are removed through multiple distillations, and vanadium oxychloride (VOCl<sub>3</sub>), which has a boiling point close to that of TiCl<sub>4</sub> (136 $^{\circ}$ C), is removed by a complexation step [11]. Because of our interest in determining whether a potentially lower cost source of TiCl<sub>4</sub> would still yield a useable grade of titanium, particularly for nonaerospace applications, a study was initiated to examine the effects of TiCl<sub>4</sub> purity on the formation, consolidation behavior, and resulting properties of commercial purity titanium powder produced by the Armstrong process. The results presented here focus primarily on differences in sinterability that were observed.

#### 2. Experimental methods

Two grades of TiCl<sub>4</sub> were obtained from the DuPont Corporation (Wilmington, DE), one which was the standard high-purity material produced for TiO<sub>2</sub> pigment manufacture (referred to as Lot I) and a second grade that was prepared using fewer purification steps (Lot II). Aliquots of each were sent to ATI Wah Chang (Albany, OR) for chemical analysis, while the bulk lots were shipped to ITP (Lockport, IL) and converted into two separate batches of cp-Ti powder via the Armstrong process described above. To minimize oxygen contamination, the resulting powder lots were packaged, shipped, and stored in argon prior to consolidation and testing.



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Element	Lot I TiCl <sub>4</sub> (ppm)	Lot II TiCl <sub>4</sub> (ppm)	Lot I powder (ppm)	Lot II powder (ppm)				
с	54	29	93	55				
N	<10	<10	77	47				
0	110	491	2400	1780				
Trace metal <sup>a</sup>	<10	506.1	<10	3220				
Na	<10	<10	330	110				
Cl	-	-	19	21				
BET (m <sup>2</sup> /g)	-	-	0.31	0.31				

 Table 1

 Results from chemical analyses conducted on the Lots I and II TiCl<sub>4</sub> precursors and cp-Ti powders

<sup>a</sup> The list of typical trace metal impurities include chlorides of: silicon, tin, aluminum, vanadium, niobium, tantalum, tungsten, tin, zirconium [12].

The particle size distribution of each was determined by sieve analysis using ASTM B214 and E11. The powders were uniaxially cold pressed at 550 MPa into MPIF-10 test bars and 4 mm × 8 mm × 25 mm long dilatometry bars. The bars were heated under 1 × 10<sup>-6</sup> Torr vacuum at 10°C/min to 1250°C and held there for a period 20 min–24 h. Density measurements of the green and sintered specimens were conducted by simple geometric and mass measurements, as well as by the Archimedes technique using distilled water as the displacement medium.

Dilatometry measurements were carried out in an Orton 1600 series dilatometer (Orton Co.; Westerville, OH) a heating rate of 5 °C/min over the temperature range of 250-1100 °C in flowing ultra-high purity argon (UHP Ar; Matheson Tri•Gas, Montgomeryville, PA). Specimen temperature was measured with an accuracy of  $\pm 1$  °C and linear dimensional changes were recorded with an accuracy of  $\pm 0.5 \,\mu$ m. After cooling, each bar was characterized by X-ray diffraction analysis to determine if oxidation occurred; specimens exhibiting measurable oxidation were not included in the final sintering analysis. Thermal analysis of the powders was conducted at Western Kentucky University using a TA Instruments differential scanning calorimetry system (DCS; New Castle, DE) equipped with a VG Thermolab mass spectrometer (MS; Thermo Scientific, Waltham, MA). All of the thermal analysis experiments were performed in flowing UHP Ar (10 ml/min) at a heating rate of 10 °C/min. Microstructural analysis of the powder and of cross-sectioned and polished sintered bars was conducted using a JEOL JSM-5900 LV scanning electron microscopy (SEM; Peabody, MA). Elemental analysis of the TiCl<sub>4</sub>, titanium powders, and sintered samples was conducted via induction coupled plasma mass spectrometry (ICP-MS) and interstitial gas analysis at ATI Wah Chang.

### 3. Results

As shown in Table 1, the chemical assays of the two grades of TiCl<sub>4</sub> exhibit relatively minor differences in C, N, and O impurity concentrations and more significant differences in trace metal impurity content. Shown in the same table, the results from ICP/MS analysis of the corresponding titanium powder lots indicate that these impurities are transferred during sodium reduction. Note that there is virtually no difference in the concentration of residual salt (NaCl) impurity in the two powders, 19 ppm for Lot I and 21 ppm for Lot II. However, there is  $3.5 \times$  more residual sodium in the Lot I powder than in the Lot II powder, 311 ppm versus 89 ppm, respectively. Engineers at ITP reported no differences in processing the two lots of TiCl<sub>4</sub> and little difference in particle morphology was observed between the two corresponding powders during microstructural analysis. As seen in Fig. 1(a) and (b), the two powders display a spongy, coral-like porous structure. The individual particles can be plastically flattened under fingertip pressure. At higher magnification, Fig. 1(c) and (d), it is apparent that both powders are actually agglomerates composed of fine scale crystallites



1mm markings



**Fig. 1.** Low magnification micrographs of Armstrong processed cp-Ti powder synthesized using: (a) high-purity TiCl<sub>4</sub> (Lot I) and (b) low-purity TiCl<sub>4</sub> (Lot II). High magnification images of: (c) high-purity Armstrong powder, and (d) low-purity Armstrong powder.



**Fig. 2**. Particle size distributions of high- and low-purity powders (Lots I and II, respectively) produced by the Armstrong process.

measuring  $\sim 3 \,\mu$ m in size. The particle size distribution for each lot is shown in Fig. 2. On average, the powder prepared from Lot I TiCl<sub>4</sub> is larger in size (809  $\mu$ m versus 438  $\mu$ m) and displays a trimodal distribution instead of a bimodal one due to the presence of a small amount of particles greater than 1680  $\mu$ m in size. However, the tapped densities of both are nearly the same, 8 and 7% of theoretical respectively for the corresponding Lots I and II powders.

In preparing the test bars, both powders compacted approximately to the same degree. The green densities of bars prepared from the Lot I powder averaged 3.86 g/cc, while those cold pressed from the Lot II powders averaged 3.78 g/cc. However, a significant difference in sintered density was observed between the two, as shown in Table 2. Both sets of bars exhibit their maximum density after sintering at  $1250 \degree C$  for  $\sim 20 \min$  and display a reduction in density (i.e. swelling) with additional time at temperature. Note that at each sintering temperature, the Lot II bars are consistently higher in sintered density even though they initially display slightly lower green densities. A comparison of the internal microstructures of both specimen types shown in Fig. 3 underscores this difference; after sintering for 8 h, compacts prepared from the Lot I powder exhibit a greater concentration of pores and larger average pore size than those fabricated using the Lot II powder. A similar phenomenon has been reported for arc-melted buttons prepared from Kroll and Hunter produced titanium sponge materials in which the salt byproduct was not fully removed. In both cases, porosity was caused by volatile species that formed during the decomposition of residual hydrated magnesium or sodium chloride inclusions during melting [13].

#### Table 2

Lots I and II bar densities after sintering at 1250 °C for 20 min, 8 h, and 24 h.

	Density (% of t	Density (% of theoretical)				
Lot	As-pressed	1250 °C, 20 min	1250 °C, 8 h	1250°C, 24h		
I	86.0	94.4	87.1	66.2		
II	84.1	96.3	90.6	71.2		

It has been previously observed that Armstrong-processed cp-Ti powder exhibits swelling when sintered under excessive conditions (i.e. high temperature and/or long soak times) [14]. In comparison, properly washed Hunter fines do not. Although the same reductant (Na) is employed in both processes, there are significant differences in the characteristics of the resulting powders. Because the Armstrong process is a continuous (not batch) method of producing titanium powder and employs a significant excess of molten sodium, the powder product contains a measurable amount of unreacted sodium that is typically removed via volatilization prior to washing away the NaCl byproduct. However, due to the lacey, coral-like morphology of the powder, it is speculated that some of the sodium may become trapped in elemental or compound form internally within closed or semi-closed voids that are generated during the reduction reaction.

By comparison, during the Hunter process TiCl<sub>4</sub> reduction takes place within a closed reaction vessel at temperatures higher than those employed in Armstrong processing. The resulting product that forms is not a powder, but a sintered spongy mass that is subsequently crushed and treated in a series of vaporization and washing steps to eliminate excess sodium and the NaCl byproduct. The sponge must then be attritted to form a powder product, although some fines are produced during the sodium reduction of TiCl<sub>4</sub>. The typical morphology of these fines is much less porous than the Armstrong powder, as shown in Fig. 4. Because of its low surface area morphology and the lack of internal voids, this powder contains very little free sodium; a typical chemical assay of Hunter fines prepared from high purity TiCl<sub>4</sub> is provided in Table 3. As mentioned above, products prepared from Hunter fines exhibit internal porosity only when the powder is not properly washed to completely remove NaCl.

DSC analysis of the Lot I material displayed no indication of an anomalous phase change or chemical reaction in comparison with a reference Kroll produced sample. However, MS analysis showed that upon heating a volatile species with an atomic weight of 44, presumed to be CO<sub>2</sub>, begins to evolve around 500 °C and that the degree of evolution increases with increasing temperature up to 1450 °C. Comparisons between chemical assays of this test specimen with the original Lot I powder indicated no significant difference in sodium content, suggesting that the residual sodium



Fig. 3. Cross-sectional SEM images of the internal microstructures of sintered bodies fabricated from: (a) high-purity (Lot I) and (b) low-purity (Lot II) Armstrong powders. Both specimens were sintered under high vacuum at 1250 °C for 8 h.



**Fig. 4.** Micrograph of Hunter processed cp-Ti fines synthesized using high-purity TiCl<sub>4</sub>.

from powder production remains even after heating to 1450 °C. The fact that sodium persists in the powder up to high temperatures and that CO<sub>2</sub> is generated during heating suggest that sodium carbonate, or a hydrated form of the compound, is the likely source of swelling. Anhydrous NaCO<sub>3</sub> is known to decompose into Na<sub>2</sub>O and CO<sub>2</sub> when heated above ~400 °C and the kinetics of this reaction increase dramatically above 1200 °C [15].

Results from dilatometry measurements, shown in Fig. 5, highlight specific differences in densification behavior observed between the two different powder lots. For example, the dilatometry curve for the Lot I material displays four primary breaks in slope; i.e. rate of expansion/shrinkage. The initial linear increase in compact length from room temperature to ~470 °C can be attributed to thermal expansion; i.e. there is no significant degree of sintering that appears to occur over this temperature range. At about 470 °C, point a<sub>1</sub>, the sample begins to shrink at a nearly linear rate up to 880 °C (point a<sub>2</sub>), a temperature close to the  $\alpha \rightarrow \beta$  transition ( $\beta$  transus) in pure titanium. At 880 °C, a sharp increase in the rate of shrinkage is observed that abruptly ends at 1010 °C (point a<sub>3</sub>).

The Lot II material also displays a low-temperature region of linear thermal expansion with the first significant measure of shrinkage occurring at ~590 °C (point b<sub>1</sub>), although it could be argued that an initial deviation from linearity might begin at 520 °C. Over the temperature range of 590–780 °C (point b<sub>2</sub>), the compact shrinks at a nearly linearly rate comparable to that of the Lot I material. It then begins to undergo a higher rate of non-linear shrinkage from 780 to ~880 °C (point b<sub>3</sub>). Beyond 880 °C, again at approximately the  $\beta$  transus, the rate of shrinkage or densification increases up to 1100 °C (point b<sub>4</sub>), then subsequently shows a gradual decline but does not abruptly halt. Panigrahi et al. reported nearly the same shrinkage behavior in micron-size cp-Ti (from pow-

#### Table 3

Results from chemical analyses conducted on cp–Ti Hunter fines produced from a high-purity TiCl<sub>4</sub> precursor.

Element	(ppm)
С	105
Ν	<20
0	1890
Trace metal <sup>a</sup>	<10
Na	1300
Cl	1400

<sup>a</sup> The list of typical trace metal impurities include chlorides of: iron, silicon, tin, aluminum, vanadium, chromium, niobium, tantalum, tungsten, tin, zirconium [12].



Fig. 5. Dilatometry curves for the compacted Lots I and II powders.

der that appears to have been formed via a hydride/de-hydride process based on the reported angular particle morphology): initial compact shrinkage that occurs at 650 °C and increases in rate at 880 °C [16,17]. They and others have suggested that low temperature sintering (<880 °C) is controlled predominantly by lattice diffusion within the  $\alpha$ -Ti [15–18]. Above the  $\beta$  transus, several mechanisms of sintering have been proposed, including pipe diffusion through dislocations, [19] lattice diffusion from surface and grain boundary sources, [20,22] and creep (via grain boundary rotation) [16].

Thus, there are two primary differences in shrinkage behavior between the Lots I and II powder compacts: (1) a difference in temperature at which sintering appears to initiate, ~470 °C versus 590 °C, respectively, and (2) a sudden cessation of shrinkage observed in the case of the Lot I material. Based on the prior powder characterization results, the key physicochemical differences between the two powder lots are: (1) a higher average particle size in the Lot I material, or more specifically a fraction of powder that is greater than 1680  $\mu$ m in size; (2) a measurably higher concentration of trace metal impurities in the Lot II material; and (3) a higher level of "free" sodium (uncombined with chlorine) in the Lot I powder. To determine the importance of the first factor, an additional set of sintering runs were conducted on the Lot I material after classifying it to exclude powder particles >1680 µm. The average green density of compacts pressed from this classified material was found to be 3.82 g/cc and the resulting densities upon sintering at 1250 °C for 20 min, 8 h and 24 h are reported in Table 4. Note that there is no significant improvement in sintered density relative to the unclassified Lot I powder (Table 2), indicating that the difference in sintering behavior between the two powder lots is impurity based.

Diffusion in  $\alpha$ -Ti is typically enhanced by group VIII transition metal elements (e.g., Fe, Co, and Ni) [21] and diminished by metal species found on either side of this region in the periodic table, e.g., Nb, Sn, and Si [22,23]. This may be one reason why sintering initiates at lower temperature in the higher purity

Table 4

Densities in bars pressed from classified Lot I powder after sintering at  $1250\,^\circ\text{C}$  for 20 min, 8 h, and 24 h.

	Density (% of theoretical)					
	As-pressed	1250°C, 20 min	1250 °C, 8 h	1250 °C, 24 h		
Classified lot I	85.1	94.2	87.3	65.9		

Lot I powder. That is, the type of trace metal impurities found in the Lot II powder delays activation of the primary mechanism for low-temperature sintering,  $\alpha$ -Ti lattice diffusion. Because the Lot I powder begins to sinter at lower temperature, closed porosity will subsequently form in the compacted material at lower temperatures as the microstructure evolves during sintering. Combined with the fact that a high-temperature, volatile compound such as NaCO<sub>3</sub> is retained on the Armstrong powders, it is this latter phenomenon that is likely responsible for the difference in sintered density observed between the two material lots. That is, swelling only occurs if the CO<sub>2</sub> becomes trapped during the sintering process; i.e. if the gas is encapsulated within a set of closed pores that form prior to significant sodium carbonate decomposition.

Because the flow stress of cp-Ti is guite low at 1250 °C (<20 ksi). the material will readily creep (i.e. swell) when subjected to an internal pressure over extended time at elevated temperature (>20 min), such as that exerted by the expanding CO<sub>2</sub> trapped within closed pores. However if decomposition occurs predominantly when the pore structure of the sintering body is effectively still open, then little to no swelling should be observed. Thus, we suspect that the higher concentration of trace metal impurities found in the Type II powder cause the delay in sintering that allows CO<sub>2</sub> to escape the compact prior to entrapment. Alloyed Armstrong titanium powder (Ti-6,4) exhibits nil swelling during sintering [14] and the mechanism responsible for this finding may be the same as that proposed here. The net effect is that the use of the lower purity TiCl<sub>4</sub> source is beneficial in two ways: (1) it is potentially a lower cost titanium precursor in the Armstrong process and (2) the trace impurities allow higher density components to be fabricated via a low-cost press and sinter approach.

#### 4. Summary

The sintering behavior of titanium powder produced via the Armstrong process from two different grades of  $TiCl_4$  was investigated by a combination of thermal, chemical, and microstructural analysis techniques. It was found that the use of lower grade  $TiCl_4$  leads to higher part density; a phenomenon attributed to a delay in the onset of powder sintering. Because of this delay, the internal microstructure of the compact remains open at higher temperatures, allowing volatiles to more freely escape and avoid becoming entrapped within the sintered body where they cause swelling/bloating during the final stages of sintering.

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