A THERMAL PATHWAY TO LOW COST TITANIUM POWDER

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PROJECT TITLE: A Novel Chemical Pathway for Ti Production to Drastically Reduce Cost
PROGRAM: Modern Electro/Thermochemical Advances in Light Metals Systems (METALS)
AWARD: $3,593,494
PROJECT TEAM: University of Utah, Arconic (formerly Alcoa) and Boeing
PROJECT TERM: February 2014 – February 2017
PRINCIPAL INVESTIGATOR (PI): Dr. Z. Zak Fang

TECHNICAL CHALLENGE

Reducing the weight of vehicles through the use of lightweight metals in place of steel is important for reducing energy consumption and emissions in the transportation sector. Unfortunately, the production of light metals is expensive and energy intensive. For example, titanium (Ti) production via the standard Kroll process consumes 100 kWh/kg, emits 36 kg CO_2/kg, and results in Ti costs of $9-10/kg before alloying or processing for parts. As a result, the use of Ti has been limited primarily to aerospace applications with very specific, high value, performance-critical parts that cannot use other, cheaper metals. Most of the cost and energy intensity associated with Ti production is associated with the difficulty in removing oxygen from the ore, and the subsequent propensity of purified Ti metal to rapidly pick up oxygen and other impurities. In the standard Kroll process, these challenges are addressed by converting Ti ore (an oxide) into $TiCl_4$, and then reducing the chloride to Ti metal with Mg. This process is both capital- and energy-intensive, as the Ti metal coming out of the reduction step must be held for over a week under a high temperature vacuum distillation, and the regeneration of Mg from the $MgCl_2$ by-product is also energy-intensive.

TECHNICAL OPPORTUNITY

With auto and aircraft manufacturers revisiting all light weighting options to improve fuel efficiency, and with the advent of 3D printing and powder manufacturing techniques for complex parts, there is a large and growing potential market for Ti powder. To meet this demand, a low energy, cost-effective means is required to produce Ti metal or manufacture Ti parts for high-volume applications. An alternative pathway that avoids chlorination of titanium oxide (TiO_2) could offer dramatically lower energy input and cost for Ti production, and potentially could expand the use of Ti into higher volume applications.

INNOVATION DEMONSTRATION

The University of Utah (Utah) project's goal was to develop a novel thermochemical process to extract Ti metal from ore that substantially reduces the cost, energy consumption, and emissions of Ti metal production. Utah's approach uses their new chemical process, which they named "hydrogen assisted magnesiothermic reduction" (HAMR). Mg has been known to be a reducing agent for TiO_2 to Ti metal. However, the equilibrium oxygen content in the Ti metal from Mg reduced TiO_2 is typically higher than 1%, depending on the temperature used, which is unacceptable for industrial applications. This is because Ti-O solid solutions can be more stable than MgO. In order to further reduce the oxygen content in Ti, Utah discovered that Ti-O can be destabilized using hydrogen[1], making it possible to turn the reduction of TiO_2 with Mg from thermodynamically impossible to thermodynamically favored. This allows TiO_2 to be reduced and deoxygenated directly by Mg to form TiH_2, with low oxygen levels that can meet the needs of the industry. TiH_2 can be further processed to Ti metal through industry standard approaches. Utah also developed a two-step technique, which is designed to overcome kinetic barriers and engineering issues. The first step of this technique is the reduction that converts TiO_2 to Ti-O solid solutions. The second step is the deoxygenation that refines Ti-O solid solutions to Ti metal with ultra-low oxygen content. The output of the process is HAMR TiH_2 powder, shown in Figure 1. This powder contains a range of particle sizes and shapes, and is suitable for subsequent sintering or other powder applications. The team reliably produced small amounts (0.2-1 kg) of the HAMR TiH_2 powder in a batch and then dehydrogenated it by heating above 400 ºC in a vacuum or inert atmosphere to produce commercially pure Ti powder (CP-Ti), and tested its purity against the industry standard for general purpose Ti composition (ASTM B299-13), as shown in Table 1. The HAMR Ti powder

[1]Zhang, Y. Fang, Z. Z., Sun, P., Zhang, T,, Xia, Y., et al. (2016). Thermodynamic destabilization of Ti-O solid solution by H_2 and deoxygenation of Ti using Mg. *Journal of the American Chemical Society*, 2016, *138:* 6916-6919.

produced from the HAMR TiH_2 powder has consistently met the purity requirements defined by the industry standard and the Utah team has developed a reliable recipe for lab-scale production of HAMR Ti powder. A 10 kg batch was produced for further testing at Utah's commercial partners, Arconic (formerly Alcoa) and Boeing.

	O	C	N	Al*	Fe	Mg	Si
HAMR	0.098	0.009	0.011	0.100	0.045	0.071	0.037
ASTM B299-13	<0.15	<0.03	<0.02	<0.04	<0.15	<0.5	<0.04

Table 1: HAMR Ti powder composition against industry standard, average of three batches (*: Al is higher than the standard, however, Ti is almost always alloyed with Al so this is not a concern.)

The deoxygenation process that Utah invented has also enabled a new means to produce high quality spherical powders of Ti and Ti-alloys, a critical and high-value feedstock for additive manufacturing ("3D printing"). Today's processes to produce spherical powders use plasmas or high temperature gases to atomize a Ti wire or rod. These processes are very expensive (>$200/kg) because the cost of the Ti wire or rod input is high, and the powder yield is low (only 20-30%, due to the wide distribution of particle size). Using Utah's new deoxygenation approach, it is now possible to form Ti spheres at about tens of micron in size by agglomerating, sintering, and then de-oxygenating smaller Ti particles (a process called granulation, sintering, and deoxygenation, or GSD). GSD can be applied to commercial TiH_2 pigment powder, or to finely ground powder from HAMR or Kroll. GSD can also use recycled Ti alloys as the raw material. Figure 1 contrasts HAMR non-spherical TiH_2 particles versus GSD spherical Ti-6Al-4V powder. The GSD process produces high quality spherical powder with a nearly monodisperse particle size distribution, suitable to feed a 3D printer. The properties of GSD powder relative to the existing industry standard are highlighted in Table 2.

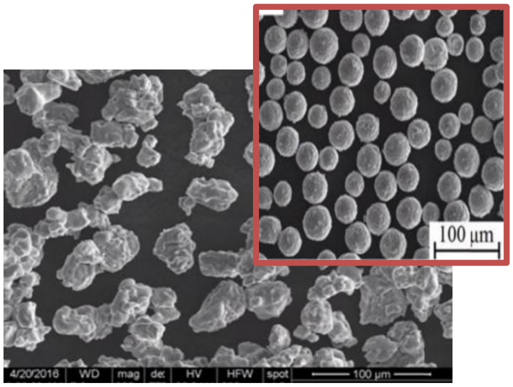

Figure 1: Non-spherical HAMR TiH_2 powder vs. spherical GSD powder.

	Density (g/cc)	O (%)	N (%)	C (%)	Al (%)	V (%)	Fe (%)	Yield (MPa)	UTS (MPa)
GSD	4.419	0.171	0.047	0.075	5.92	4.48	0.33	1059	1105
Commercial powder for Selective Laser Melting (SLM)	4.414	0.204	0.087	0.016	6.38	4.52	0.47	1074	1132
ASTM F2924	--	<0.20	<0.05	<0.08	5.50-6.75	3.50-4.50	<0.30	825	895

Table 2: GSD powder alloy composition and properties against industry standard and incumbent technology (laser-sintered) (UTS: Ultimate tensile strength)

To assess the commercial viability of the HAMR process, Utah performed a techno-economic analysis and a full process simulation in ExtendSim (a well-known chemical processing simulation software) to estimate the energy consumption, emissions, and cost at mass production. The modeling effort included the feed materials, reaction conditions (temperature and pressure), and side processes (pretreatment of the feed materials and post-treatment of the products). As shown in Figure 2, the HAMR process is 50% less energy intensive and generates 30% less emissions than the Kroll process, even after accounting for an additional purification step of the TiO_2 feed prior to the HAMR process. The bulk of the energy and emissions savings comes through eliminating the need to chlorinate TiO_2 to make $TiCl_4$, and vacuum distillation after the reduction of $TiCl_4$. For the GSD process, the improved yields from this new pathway allows for production to occur at more than 50% lower cost, dramatically lowering the potential price point of high quality Ti powder while keeping energy usage and emissions comparable to the state of practice.

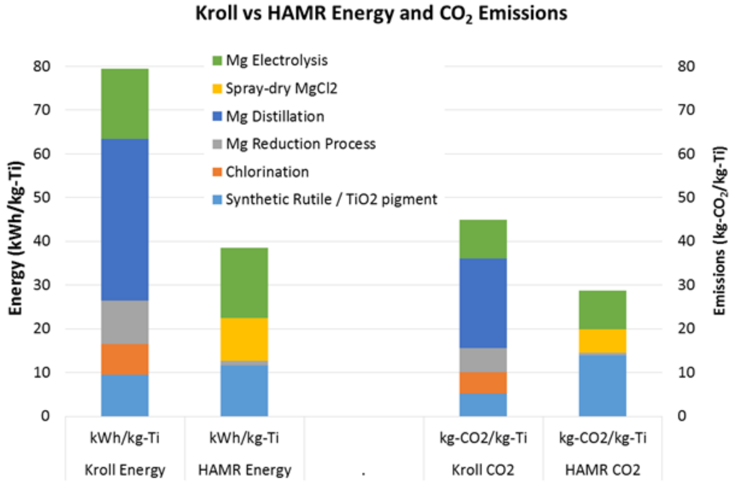

Figure 2: Energy and CO_2 benefits of HAMR vs. Current Ti Production Processes

PATHWAY TO ECONOMIC IMPACT

The key challenge for moving forward is scaling up the HAMR and GSD processes from lab-scale demos (~kg batches) to commercial-scale production (thousands or tens of thousands of tons annually). In scale-up there will be many engineering issues in thermal management, reactor design, and system integration that must be overcome and optimized. In addition to obtaining industrial validation of the Ti powders, more samples and parts of much larger sizes must be demonstrated and tested. Utah is working with its partners, Boeing and Arconic, to design new scope and testing protocols that will allow the team to fully scale and validate their products over the next two years. Their goal is to improve their HAMR process for higher volume production of CP-Ti for higher volume markets.

Utah's success with the GSD process for spherical powders offers an ideal first market, with a high-value product for the rapidly growing additive manufacturing industry. The GSD process offers a fast path to scale for this market, and the unique ability to produce custom alloys in small batches for customers to test and improve their 3D printing performance. Utah has spun out a small company, FTP Technologies, to pursue this market. The market size for spherical Ti is expected to reach 2,000 tons in ten years, but faster growth is possible with the lower cost feedstock and improved performance of alloys from the GSD process.

LONG-TERM IMPACTS

Ultimately, if the HAMR process proves to be scalable, it is projected to reduce the price of Ti parts by 50% or more. It is too soon to determine whether HAMR could drive the price of Ti low enough to displace steel for widespread use in high volume automotive applications, but it does show the promise to dramatically alter the Ti market and increase the range of applications for high performance, lightweight Ti parts. The team projects that its HAMR process could generate billets for automotive and other large scale use at a scale of around a million tons per year, potentially displacing millions of tons of heavier stainless steel products over time.

INTELLECTUAL PROPERTY AND PUBLICATIONS

As of December 2016, Utah has generated two invention disclosures to ARPA-E, two U.S. Patent and Trademark Office (PTO) patent applications, and one patent.

Patents

Zhigang Zak Fang, Yang Xia, Pei Sun, Ying Zhang. Production of substantially spherical metal powders, US patent 9,421,612 B2.

Publications

Utah has also published the scientific underpinnings of this technology extensively in the open literature. A list of publications is provided below:

Zhang, Y., Fang, Z. Z., Xia, Y., Sun, P., Van Devener, B., Free, M., Lefler, H. & Zheng, S. (2017). Hydrogen assisted magnesiothermic reduction of TiO_2. Chemical Engineering Journal, 308, 299-310.

Sun, P., Fang, Z. Z., Xia, Y., Zhang, Y., & Zhou, C. (2016). A novel method for production of spherical Ti-6Al-4V powder for additive manufacturing. Powder Technology, 301, 331-335.

Zhang, Y., Fang, Z. Z., Sun, P., Zhang, T., Xia, Y., Zhou, C., & Huang, Z. (2016). Thermodynamic Destabilization of Ti-O Solid Solution by H2 and Deoxygenation of Ti Using Mg. Journal of the American Chemical Society, 138(22), 6916-6919.

Zhang, Y., Fang, Z. Z., Xia, Y., Huang, Z., Lefler, H., Zhang, T., Sun, P., Free, M.L. & Guo, J. (2016). A novel chemical pathway for energy efficient production of Ti metal from upgraded titanium slag. Chemical Engineering Journal, 286, 517-527.

Cho, J., Roy, S., Sathyapalan, A., Free, M. L., Fang, Z. Z., & Zeng, W. (2016). Purification of reduced upgraded titania slag by iron removal using mild acids. Hydrometallurgy, 161, 7-13.