Production of fine titanium powders via the Hydride-Dehydride (HDH) process

Titanium powders have been used successfully in a wide range of near shape PM applications, and in recent years the demand for finer titanium powders for PIM applications has increased significantly. Dr Colin McCracken and Dan Barbis of Reading Alloys Inc. review the latest developments in the manufacture of finer titanium powders using the hydride-dehydride (HDH) process. They also review the impact of raw materials and particle size distribution on both the powder morphology and powder chemistry.

'titanium alloys exhibit both high strength and low density... ideally suited for aerospace and other applications'

Reading Alloys Inc. (RAI) has been one of the leading producers of master alloys for over 50 years, and is well known in both the titanium and aerospace industries. Master alloys are typically supplied in the size range of 6.3mm to 300µm and are used, for example in the production of titanium alloys by providing aluminium, vanadium, tin, molybdenum, chromium, and iron alloying elements [1]. These titanium alloys exhibit both high strength and low density, which make them ideally suited for aerospace and other applications. Titanium and its alloys also exhibit other important characteristics, such as high corrosion resistance and very good biocompatibility, and are also used extensively in implantable medical applications [2-3].

The majority of high purity fine titanium powders used for powder injection moulding applications are produced by a gas atomisation process, which results in spherical powder particles with a narrow particle size distribution (PSD) range. This review will explore an alternative powder manufacturing process referred to as the Hydride-Dehydride (HDH) process. Unlike the gas atomisation process, which produces a near-final PSD, the HDH process is used to resize large titanium pieces down to a finer PSD through crushing, milling and screening. The resulting high purity, finer titanium powder can have a similar PSD to atomised powder, but a very different morphology. The morphology of the final powder is also directly impacted by the starting raw materials. We will also review the impact of the starting raw material on

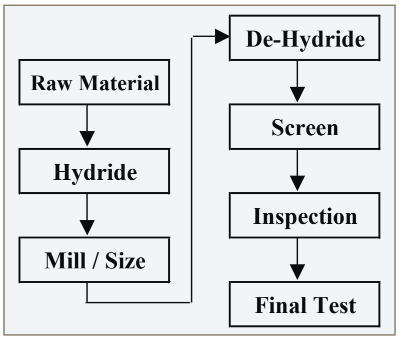

Fig.1 Flow diagram of the HDH process

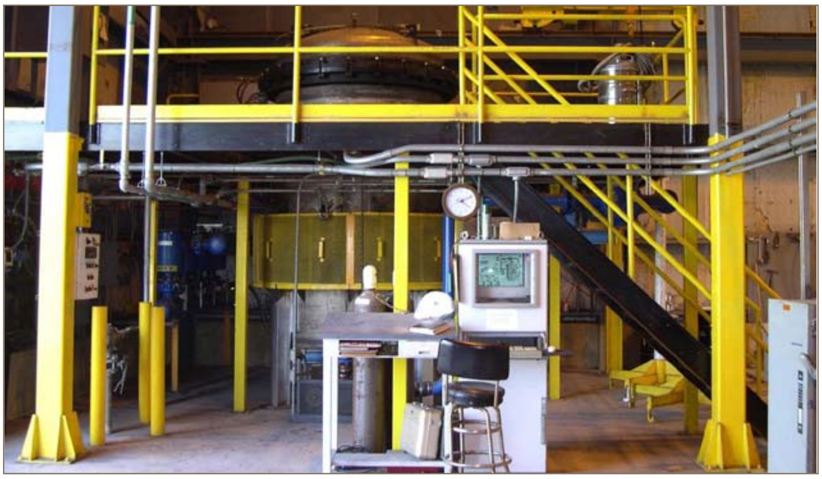

Fig. 2 RAI's production HDH unit.

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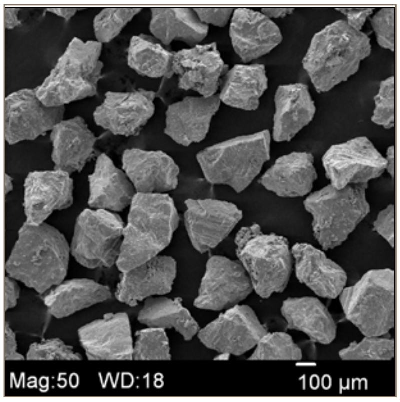

Fig. 3 SEM image (x50) of coarse HDH Ti powder produced from wrought titanium feedstock screened to 212-300µm

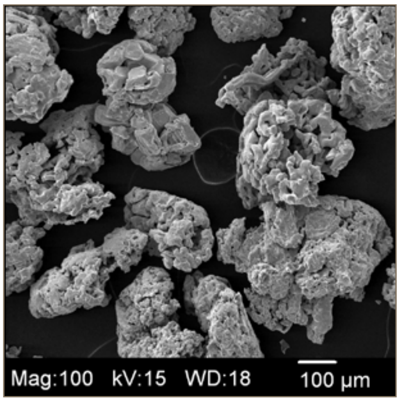

Fig. 4 SEM image (x100) of coarse HDH Ti powder produced from sodium reduced sponge powder screened to 212-300µm

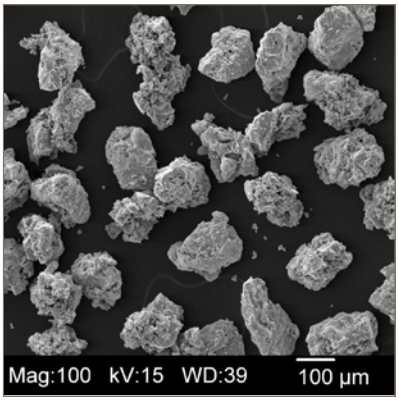

Fig. 5 SEM image (x100) of coarse HDH Ti powder produced from magnesium reduced sponge powder screened to 212-300µm

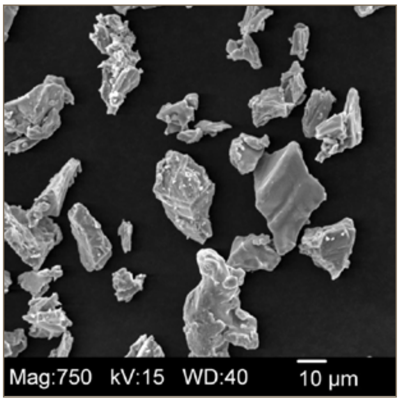

Fig. 6 SEM image (x750) of coarse HDH Ti powder produced from wrought titanium feedstock screened to <25µm

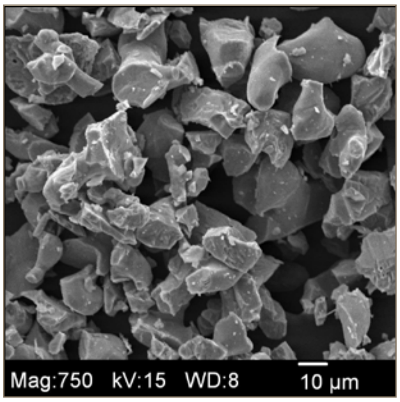

Fig. 7 SEM image (x750) of coarse HDH Ti powder produced from sodium reduced sponge powder screened to <25µm

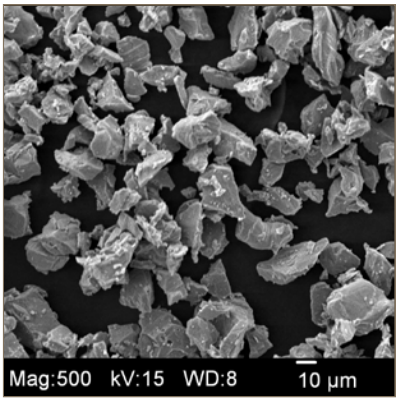

Fig. 8 SEM image (x500) of coarse HDH Ti powder produced from magnesium reduced sponge powder screened to <25µm

the chemistry and particle size distributions of screened powder fractions.

Manufacturing route

RAI's manufacturing procedure is based on the Hydride-Dehydride (HDH) process, which relies upon the brittle nature of some metal hydrides that can then be milled and screened to produce finer powders. Fig. 1, shows a flow diagram of the manufacturing process. Titanium raw materials are initially loaded into a hydride unit, (Fig. 2) and heated under a hydrogen atmosphere for approximately 4 days. Titanium and hydrogen react to form titanium hydride (TiH_2). The brittle TiH_2 is allowed to cool down under the hydrogen atmosphere before being removed from the hydride unit. TiH_2 can then be readily crushed and sized down into a fine hydride powder.

The TiH_2 powder is screened to meet the individual PSD requirements of each customer. Sized TiH_2 powder is then returned to the hydride unit for dehydride. The powder is again heated and under a high vacuum the hydrogen is removed from the titanium in a reversible reaction, as shown in the following equation:

$$Ti\ (solid) + H_2\ (gas) \leftrightarrow TiH_2\ (solid)$$

Material	Sodium	Magnesium	Carbon	Hydrogen	Nitrogen	Oxygen
Mg-reduced Ti Sponge Powder	0.0001	0.015	0.011	0.013	0.042	0.44
Wrought Ti Powder	0.0001	0.005	0.032	0.011	0.022	0.34
Na-Reduced Ti Sponge Powder	0.05	N/A	0.057	0.015	0.027	0.32

Table 1 Typical Chemistry for different <25µm Titanium raw materials.

Titanium dehydride powder is then re-screened through check screens to remove any powder particles that may have sintered together during dehydride and then submitted for certification. RAI is accredited to ISO 9001:2000 and holds certification for its NADCAP approved test laboratories. The finished lot is packed in accordance with specific customer requirements and exported worldwide according to international agreed transportation standard for shipping hazardous materials.

Titanium powder morphology

As outlined in the introduction, final powder morphology is strongly impacted by the starting raw materials. There are currently three high volume sources of titanium raw materials, wrought titanium feedstock, sodium reduced sponge powder and magnesium reduced sponge powder (Kroll Process) [4]. The wrought titanium is produced by vacuum melting sponge powder.

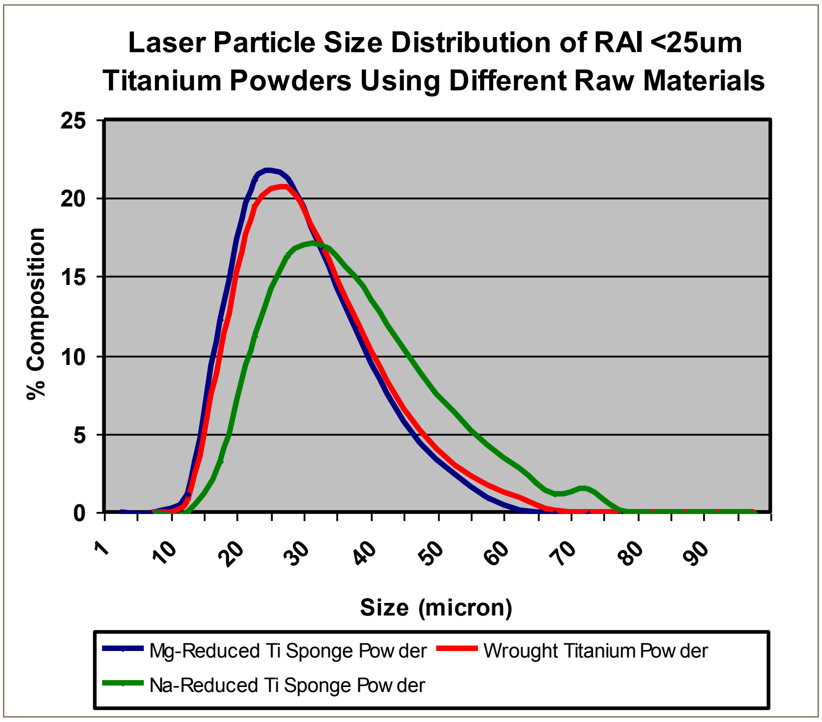

Fig. 9 Typical Malvern (laser) PSD curves for different titanium raw materials

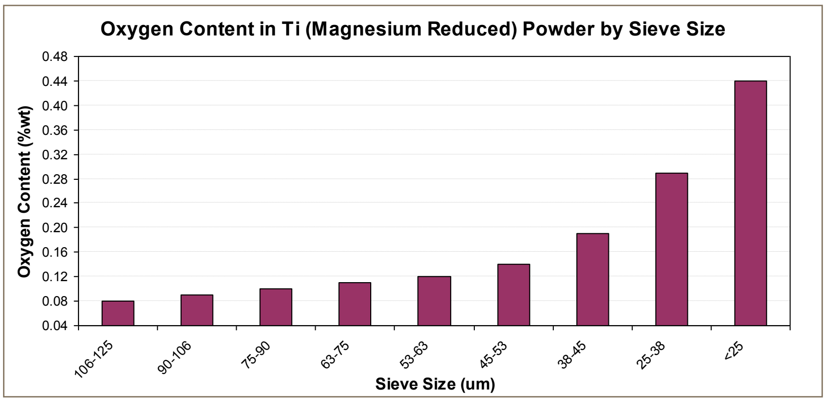

Fig. 10 Typical Oxygen content as a function of PSD for Magnesium reduced Titanium sponge

Continued milling of these three different raw materials produces smaller and smaller powder particles, which also results in a convergence of particle morphologies, shown in Figs. 6-8.

The PSD for each powder type will differ slightly as a function of how each material interacts with the crushing and milling process, as shown in Fig.9. Both wrought and magnesium reduced titanium sponge powders have similar PSD ranges, but the sodium reduced titanium sponge particles are more elongated, resulting in broader PSD range when mechanically screened.

Titanium powder chemistry

Samples from each of the three different (starting raw materials) <25µm powders were analysised for chemistry, as shown in Table 1.

For titanium, gas contents are very important parameters as they can affect the mechanical properties of the finished product [5]. For finer HDH titanium powders the oxygen content is dominated by the powder surface area to volume ratio. As the particle diameter decreases the powder surface area to volume ratio increases significantly. Titanium like many other metal powders exhibits a surface passive oxide film, i.e. titanium dioxide, therefore as the mean particle diameter decreases the oxygen content increases, as shown in Fig.10. Careful selection of the PSD for very fine powder can significantly impact the final chemistry of the finished powder.

Summary

Reading Alloys Inc. has been an approved titanium powder supplier to both the medical coating and sputtering target industries for many years. Not all titanium powders are the same as outlined in this paper. Both the starting raw material and particle size distribution can significantly impact morphology and chemistry of the final powder product. Reading Alloys offers its customers both standard and custom titanium powder formulations for their specific applications. In recent years there has also been an increased demand for titanium hydride powders, which Reading Alloys offers as an intermediate manufacturing product. As the number of near net shape applications for titanium powders continues to increase, Reading Alloys has embarked on a significant HDH expansion program for 2008 as outlined in the September 2007 issue of *PIM International* [6].

References

[1] www.reading-alloys.com
[2] K. L. Housley (ed), Black Sand, The History of Titanium, ISBN: 0-935297-43-X, 2007, 110-121
[3] J.R. Davis (ed), ASM Specialty Handbook: Materials for Medical Devices, 3rd Edition, ISBN: 0-87170-790-X, 2005, 38-50
[4] William J. Kroll, "How Commercial Titanium and Zirconium Were Born", Journal of The Franklin Institute, Sept 1955, 179
[5] ASTM Standard Specification for Titanium and Titanium Alloy Bars and Billets, Designation: B 348-06a, June 2006,
[6] Industrial News. Powder Injection Moulding International, 2007, 1(3), 6

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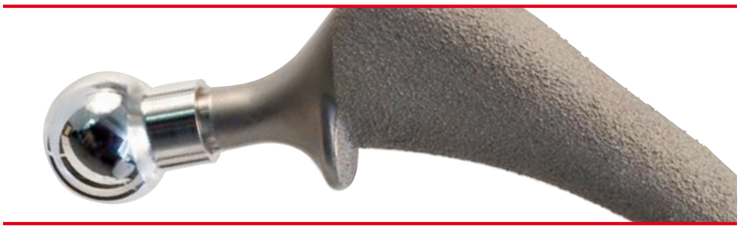

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FINE METAL POWDERS

Reading Alloys, Inc. is a global leader in the design, development and production of specialty alloys products including a new range of high-purity fine metal powders suitable for PIM and MIM applications.

PRODUCTS

Low Oxygen CP Ti and Ti-6Al-4V, Al-V, Mo-Ti and Nb powders. Metal and alloy hydride powders are also available.

APPLICATIONS

For PM, PIM and MIM components such as medical devices.

CHARACTERISTICS

Hydride-Dehydride (HDH) powders with controlled particle sizes from <45 microns to <25 microns.

NEW PRODUCTION FACILITY

25,000 sq. ft. state-of-the-art facility. Powders available for pilot trials to full-scale production.

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