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This article provides a concise overview of current powder metallurgy (PM) activities in Australia and important developments to date. The overview is concerned primarily with the conventional PM of titanium and titanium alloys. It also cites rapidly growing additive manufacturing (AM) activities in Australia. The article concludes with brief history, current activities, and future plans regarding PM titanium in New Zealand.

POWDER METALLURGY IN AUSTRALASIA

Ma Qian,* John E. Barnes, Mark Gibson*** and Brian Gabbitas******

INTRODUCTION

Current PM activities in Australia focus primarily on titanium, and this environment is likely to continue in the foreseeable future. The rationale for this development is that some of the most valuable resources of titanium-bearing ore on the planet are found in Australia, while Australia participates only in the lower end of the value chain. Ore and pigment are an order of magnitude less valuable than titanium metal. Although titanium and titanium alloys are the materials of choice for a wide range of applications, the cost-affordability issue has limited their usage to just a few industries on a small scale. PM offers a cost-effective approach for the fabrication of titanium and titanium-alloy components. This article provides a concise overview of the current PM titanium activities in Australia and New Zealand and the important developments made to date.

TITANIUM AND TITANIUM-ALLOY POWDER PRODUCTION

The Commonwealth Scientific and Industrial Research Organisation (CSIRO) is Australia's national science agency and has been engaged in developing a number of innovative activities and processes to add value to a prime resource ("from ore to more") through the Titanium Technologies Theme within the CSIRO's Future Manufacturing Flagship program. Two patented production processes have been developed to produce metallic-powder feedstock.

One patent covers the direct production of alloys based on the titanium–aluminum system via a two-step aluminothermic reduction of titanium tetrachloride ($TiCl_4$).[1] In the first step, $TiCl_4$ is reduced by aluminum to titanium trichloride ($TiCl_3$) at a temperature below the boiling point of $TiCl_4$ and at one atmosphere under argon. The resulting $TiCl_3$ intermediate product is then reacted with aluminum powder at temperatures up to 1,000°C, leading to the synthesis of a titanium–aluminum alloy powder used as a feedstock for further downstream processing.

Similarly, the TiRO™ process has been developed for the continuous direct production of commercially pure (CP) titanium powder.[2] This process also has two main processing steps: a reaction step in which titanium metal is produced in the form of very fine particles dispersed within larger composite

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particles also containing magnesium chloride ($MgCl_2$). The $MgCl_2$ is then separated from the titanium powder in a continuous-vacuum distillation unit. The titanium product from this unit comprises a lightly sintered "biscuit" of titanium particles that can be broken up into individual powder particles with a D_{50} ~200 μm. These particles have a unique morphology that is a function of the process. For many PM applications TiRO powder requires further processing to tailor its morphology for specific applications.

CSIRO is developing powder manipulation technology to modify TiRO particulates to improve density, flowability, size, size distribution, and shape suitable for PM and AM, via powder-bed and blown-powder techniques, and for cold-spray technologies. In addition, there are other research activities that target the development of new alloys, which are tailored to the unique characteristics of the two powder production processes. This will also provide significant benefits to the final product/component resulting from the various powder consolidation and AM technologies under investigation.

TITANIUM POWDER ROLLING AND EXTRUSION

CSIRO is working on the development of continuous processes for the manufacture of titanium and titanium alloy semi-finished mill products from powder feedstock. It has two patented technologies under commercialization. In the first process, powders are compacted by cold rolling to form a green strip.[3] This direct powder rolling (DPR) process uses cold metal powder that is fed vertically into a set of horizontally positioned symmetrical rolls. The process compacts the powder into a green sheet that is 75%–80% of the pore-free density. The green strip is fed to an inductively heated graphite furnace where it is preheated rapidly in an argon atmosphere for a few minutes and then transferred, in a continuous manner, to a hot-rolling station.

A characteristic of the combination of DPR and hot roll densification (HRD) is the short preheating time prior to hot rolling, which results in significant benefits in productivity. This process is capable of producing strip from CP-titanium powders, prealloyed powders, and mixed elemental powders. It has been on trial with a wide range of titanium powder morphologies. Most of the development work has been conducted with binderless free-flowing hydride/dehidride (HDH) powders. Another important advantage is that both CP-titanium-grade strip and titanium-alloy strip can be manufactured to a thin gage (<1 mm) in one or two hot rolling passes. This significantly reduces material waste, especially the yield loss resulting from surface-removal treatments. The strip exits from the hot-consolidation rolls, fully dense, directly into a cooling chamber that is also purged with argon to minimize the pickup of atmospheric gases. In this condition, the strip exhibits a typical hot-worked microstructure. After appropriate post-consolidation processing and/or a mill anneal the microstructure is recrystallized and properties comparable with those of wrought CP-titanium are obtained. Fabrication of fully consolidated sheet that meets the ASTM B265 specifications has been demonstrated.[4] The degree of sintering between powder particles, post-processing density, and the particle-to-particle boundary layer (where compositional variations may exist), have a significant effect on the ability to form the sheet into useful components. These factors are currently under investigation to optimize the process.

The second technology is a continuous titanium rod/wire-forming process. The advantage of such a process is that it offers the potential for producing rod and narrow-gage wire directly from rod and powder feed and eliminates or reduces the multiple production stages characteristic of conventional titanium rod/wire fabrication. Arguably, the most economic promise for the continuous extrusion of titanium is from a continuously free-flowing and low-cost powder feed, particularly for narrow-gage wires where, for gages <1 mm, price increases almost exponentially.

Applications for continuous titanium extrusion need not be confined to traditional uses. Specialty wire fabricated as feed to AM processes, such as the Sciaky wire-based electron beam AM system, offers exciting possibilities. The continuous extrusion of titanium and its alloys from elemental mixes is possible using a modified 175kW BWE Conform 285 machine with suitably modified tooling. In order to achieve extrusion it is necessary to preheat the titanium feed and to preheat the extrusion tooling with subsequent forced cooling to maintain steady-state tooling temperatures. CP-titanium (Grade 2–3) was extruded from both cold isostatically pressed (CIPed) rod and flowing pelletized feedstock derived from HDH powder (-100 mesh). The argon purge through the metal-flow path of the extruder kept the oxygen pickup due to the extrusion operation to 0.02 w/o to 0.03 w/o. In general, this ensures that the CP-titanium grade was maintained from feed to product in terms of the oxygen content. The density of the product was also high. CP-titanium (Grade 3) wires exhibit tensile properties that are better than those of generic extrusions for 6 mm dia. wires; this is probably due to the grain-refined microstructures in the as-extruded condition. The wires respond to a mill anneal that may be of value for additional post processing.

Extrusions were also successfully fabricated from novel-powder feeds. These powders may be processed as per HDH feeds with some additional preconditioning. Extrusions produced from these powders have microstructures similar to those in material fabricated from HDH powders, which bodes well for other irregularly shaped powder feeds that may be used for this process. Mixed or blended elemental feedstocks offer both cost savings and forming advantages over alloy feed, but require post-processing treatments. The continuous production of titanium rod/wire has been proven to be feasible, but requires scale-up of the feed delivery systems for either flowing powder or precompacted feeds.

NET-SHAPE MANUFACTURING BY COLD-SPRAY FORMING

Cold-gas dynamic spraying (cold spraying) is a process that has been used for applying coatings to surfaces. CSIRO has developed an innovative cold-spray process for the net-shape fabrication of seamless pipes and load-bearing structures of titanium and/or titanium alloys.[5,6] This innovative use of cold spraying simplifies the process with attendant economical advantages. In particular, it avoids the need to weld titanium components together. Details of these two inventions have been disclosed in two recent patents.[5,6]

FUNDAMENTAL UNDERSTANDING AND DESIGN OF PM TITANIUM ALLOYS

The Australian Research Council (ARC) has provided strong support for the R&D activities of PM titanium in Australia since 2005 through its Centre of Excellence for Design in Light Metals and Linkage Project Programs. The latter program provides funding to support R&D projects involving collaboration between higher-education researchers and industry. The major PM titanium R&D activities supported under these two programs include (i) design and development of cost-effective PM titanium alloys; (ii) scavenging of oxygen, chlorine, and other impurities from inexpensive HDH titanium powder; (iii) consolidation of titanium powder by both conventional and innovative means; (iv) titanium metal injection molding (MIM) using nonspherical titanium powder; (v) deformation processing of titanium powder and preforms for novel-alloy development and enhanced performance; and (vi) development of novel titanium microstructures by severe plastic deformation, and the modelling of powder compaction. The research outcomes, which have been published widely, provide an improved basis for the design and fabrication of novel PM titanium alloys. Notable findings include:

- Rare-earth oxides are effective scavengers of chlorine from titanium powders; a small addition could enhance sintering densification significantly.[7,8]
- Rare-earth silicides can be used to effectively scavenge both oxygen and chlorine from titanium to improve sintered density and ductility.[8] The operative mechanisms when rare-earth elements are introduced depend on the form and mode of addition.[7–10]
- As-sintered beta-titanium alloys (titanium–molybdenum and titanium–niobium) are extremely sensitive to the (impurity) carbon content. The presence of 0.03 w/o C, though much less than the specified 0.08 w/o C maximum,[11] can lead to noticeable grain-boundary titanium carbides.[12]
- A critical oxygen level (around 0.33 w/o) exists in order to exhibit tensile ductility in as-sintered Ti-6Al-4V.[13,14] Beyond this level, oxygen leads to microstructural changes that are responsible for the much-reduced tensile ductility.[15]
- The sintering densification of titanium alloys is determined by the self-diffusion of titanium, which is affected by the alloying elements. Microstructural development is determined by the diffusion of the alloying elements.[16]

These fundamental findings have served as the basis for the design and development of several low-cost sinterable PM titanium alloys in Australia. When sintered using inexpensive -100 mesh HDH titanium powder, these alloys exhibit tensile properties clearly above the ASTM B381-10 specification for Ti-6Al-4V forgings. The cost of producing an as-sintered titanium alloy part is estimated to be close to that of a PM stainless steel part in terms of the part volume.

CURRENT COMMERCIAL PM OPERATIONS IN AUSTRALIA

Advanced Metallurgical Solutions (AMS), based in Adelaide, and Coogee Energy Pty Ltd., based in Melbourne, are the two prime companies that deal with PM. AMS offers high-value products based on state-of the-art sintered-metal manufacturing technology as well as engineering, design and development services, and system integration. The main business areas of AMS are microfiltration and MIM. For microfiltration, AMS produces tubular and sheet metallic filtration membranes, modules, arrays, and complete systems in a variety of alloys and separation grades, with the core parts being manufactured by sintering. The main industrial sectors served include water and wastewater, chemical production, food and beverage, pharmaceutical, mineral processing, biofuels, pulp, and paper. For MIM, AMS produces high-value MIM stainless steel, titanium, and other metal parts. Coogee Energy's current PM business deals mainly with titanium powder production based on the TiRO and further processing of the titanium powder for specific applications.

ADDITIVE MANUFACTURING OF METALS

In September 2010, Wohlers Associates was commissioned by the CSIRO to create an industry-aligned AM (3D printing) technology roadmap for Australia. Its focus was to be on metals with particular emphasis on titanium. The roadmap was completed in March 2011. Since approximately 2010, the AM of metals has attracted significant investment in Australia, led by the CSIRO, Monash University, and RMIT University, all based in Melbourne. In order to make effective use of 3D printers and assist Australian manufacturing companies to compete globally, CSIRO has recently initiated the Australian Additive Manufacturing Network to facilitate collaboration between research organizations and industry. A number of AM projects are being carried out across Australia, funded by government, industry, and the private sector. For instance, Monash University and CSIRO are working together to manufacture a small engine utilizing AM technology. The Australian Defence Materials Technology Centre (DMTC) and selected industry partners are undertaking a titanium AM benchmarking study, and RMIT University is working with an industrial partner to make Inconel 718 blades using the technology. In light of the interest in AM, a significant increase in R&D activities in AM is expected in Australia in the near future.

PM TITANIUM IN NEW ZEALAND

R&D involving PM titanium in New Zealand (NZ) started in 1998 with the formation of Titanox Development Ltd. This is a spin-off company based on a novel process invented at the University of Waikato for making titanium-base composite materials. Funding for PM titanium R&D from the New Zealand Government began in 2000 through the Foundation of Research Science and Technology (FoRST). The total (approximate) funding to date for R&D PM titanium from the Government is >NZ$12 million, which has been distributed primarily to the University of Waikato, the Titanium Industry Development Association (TiDA), and Titanox.

Current major research activities on PM titanium in NZ include: (i) titanium and titanium-alloy powder production (Titanox), (ii) titanium-powder-compact forging and extrusion (Waikato), (iii) development of new coating processes for titanium and titanium alloys (GNS Science), (iv) MIM titanium (TiDA, Waikato, and Auckland), (v) design and development of cellular titanium structures (Callaghan Innovation), and (vi) AM of titanium alloys (TiDA). The important outcomes to date are: (i) an innovative titanium-powder production method, (ii) an economical titanium-powder compact-consolidation technology by forging and extrusion, which is beginning to draw interest from industry, and (iii) commercial contracts for laser-sintered titanium parts. The near-future plan is to transfer developed technologies for powder-compact forging and extrusion to NZ industry, to further develop and grow the AM business for titanium and titanium alloys, and to develop novel cost-effective PM titanium alloys with good strength, ductility, and fracture toughness.

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