Titanium Sheet Fabricated from Powder for Industrial Applications

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In collaboration with Ametek and Commonwealth Scientific and Industrial Research Organization (CSIRO), Oak Ridge National Laboratory has evaluated three different methods for converting titanium hydride-dehydride (HDH) powder into thin gauge titanium sheet from a roll-compacted preform. Methodologies include: sintering, followed by cold rolling and annealing; direct hot rolling of the roll-compacted sheet; and hot rolling of multiple layers of roll compacted sheet that are encapsulated in a steel can. Fabrication of fully consolidated sheet has been demonstrated using all three methods and each processing route has the ability to produce sheet that meets ASTM B265 specifications. However, not every method currently provides sheet that can be highly formed without tearing. 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 components. Uniaxial tensile test results, compositional analysis, bend testing, and biaxial testing of the titanium sheet produced from hydride-dehydride powder will be discussed. Multiple methods of fabrication and the resulting properties can then be assessed to determine the most effective and economical means of making components for industrial applications.

Aerospace Dependence of Titanium and Alternate Processing Examined

Titanium (Ti) and its alloys have many superior properties compared to other metals used in industrial applications, including: high corrosion resistance, ductility, and very good strength-to-weight ratios [1,2,3,4]. The latter attribute makes it compelling for use in aerospace applications. The erratic supply and wide price swings associated with aerospace uses of titanium have the effect of relegating titanium to the status of an exotic material [2,3]. Industrially, titanium is often considered as a last resort; when nothing else will work. If the production of titanium for use in industrial applications such as petroleum refining, chemical processing, pulp and paper processing, condenser tubes, vehicle components, and heat exchangers could be decoupled from the aerospace sector, economic compromises could be made based on a balance between performance and cost. The ongoing expansion of industrial uses for titanium is driven by reduced maintenance intervals, longer service life, and component mass reduction, all of which increase energy efficiency and improve the competiveness of U.S. industry.

In 2007, the Department of Energy funded an independent study to evaluate "Industrial Markets for Titanium Manufacturing". The study included overall energy consumption and the impact of lower cost processing methods for making titanium [5]. The report was not made public, since proprietary information was included. The two product areas that were identified as having the largest potential benefit (i.e., price and energy) by starting with Ti powder and using powder metallurgy consolidation methods were thin gauge Ti sheet and net shape components with complex geometries. In these areas, conventional Ti manufacturing processes result in low yields and require high labor input. An Oak Ridge National Laboratory study performed in 2011 confirmed the independent study's findings [6]. The overall outcome from these two reports has been a sustained and concentrated research effort on developing 1) affordable thin gauge commercially pure (CP) Ti sheet, and 2) development of powder metallurgy and additive manufacturing methodologies for manufacturing complex net shapes.

Most aerospace applications of Ti require the unequivocal surety of properties defined in the Metallic Materials Properties Development and Standardization (MMPDS) handbook. Often, for industrial applications, the most significant mechanical property requirement for Ti sheet is in formability to produce the finished component, not in the mechanical performance in-service. With limited mechanical requirements, and therefore less qualification rigor, production of industrial sheet metal titanium can follow an alternate manufacturing route, resulting in potential cost savings. For example; heat exchanger plates are approximately 0.5 mm thick and operate with very little pressure and/or mechanical loads during service. High ductility in the titanium sheet is required to accommodate the deformation imparted by steel dies that shape the channels necessary to accomplish heat transfer in service. However, in the final application, the principal properties required of the sheet are to conduct heat, separate fluids (non-porous), and remain corrosion resistant. Hence, flat plate heat exchanger applications are a natural entry point for titanium of lesser mechanical performance than that of aerospace grade materials.

For the last seven years, ORNL has conducted research and development on the fabrication of titanium sheet from solid state produced powder with the goal of producing Ti sheet with physical properties suitable for industrial application at a lower cost than the current sheet made by conventional ingot metallurgy [7]. The effort has been focused on developing a low cost method for producing thin gauge titanium sheet via roll compaction followed by sintering and cold rolling or hot rolling. The sheet is suitable for use in heat exchangers, desalination units, chemical apparatus, and other industrial applications. Both the consolidation process and the feedstock production are independent of the conventional ingot metallurgy titanium processing route used for aerospace applications and, therefore, are less susceptible to the cyclic titanium market which can result in high prices and long product delivery lead times. This report describes the evaluation of magnesium reduced titanium hydride-dehydride (HDH) powder that was roll compacted at Ametek and then fully consolidated by one of three methods: 1) sintering and cold rolling until fully consolidated, 2) hot rolling in an inert atmosphere at CSIRO, or 3) multilayer stacking in a steel can followed by hot rolling. These three methods were chosen based on an evaluation of the industrial infrastructure currently required to produce Ti sheet and also with consideration of building a unique manufacturing infrastructure that would optimize the process as the markets expand.

Consolidation and Thermo-Mechanical Processing of Powder

Commercially pure, grade 2, hydride-dehydride (HDH) titanium powder was purchased and characterized to determine its suitability for roll compaction. The powder attributes are shown in Table I. Figure 1 is a scanning electron microscope image that shows the morphology of the as-received powder.

Ametek Inc. (Wallingford, CT) added a proprietary binder to the powder and performed roll compaction into 380 mm wide partially consolidated sheet nominally 2.5 mm to 2.9 mm thick and 75 to 85 percent dense.

The roll compacted sheet had the binders removed via a low temperature (<300°C) combination vacuum / inert gas bake out. Once the partially consolidated sheet had the binder removed, the three aforementioned processing routes were used to fully consolidate the sheet with the intent of identifying the most effective and economical consolidation method. The details of the three processes are as follows:

Process route 1 (PR1): After the binder removal process, vacuum sintering at 1,100°C was performed, followed by cold rolling. A total of five vacuum sintering / cold rolling cycles were required to produce 1 mm thick sheet. A final anneal at 800°C for 1 hour was performed on the sheet after the last cold rolling cycle to achieve desired mechanical properties.

Process route 2 (PR2): After the binder removal process, vacuum sintering at 1,100°C was performed, followed by hot rolling in an inert atmosphere rolling mill, where the sheet was preheated above the beta transus (> 880°C) and immediately reduced in a single pass to full density. The processing route was similar to previous descriptions of CSIRO’s hot rolling sheet fabrication method [8,9]. At the completion of rolling, the strip was chemically etched in a nitric acid / hydrofluoric acid solution to remove surface contaminants. Following etching, the material was ground to a 1 mm thickness for property testing.

Process route 2A (PR2-A): Identical to PR2 except that a heat treatment at 800°C for 1 hour in an air furnace followed by air cooling was performed prior to grinding. This replicates the typical industrial practice for aerospace grade Ti sheet.

Process route 3 (PR3): Following the binder removal process, the roll compacted sheet was stacked in 20 layers in a picture frame style carbon steel can. The can was evacuated, weld closed, and hot rolled at 950°C to 13 mm at Niagara Specialty Metals (Akron, NY). The steel can was removed and the 13mm thick plate was heated to 950°C in a natural gas fired furnace and further hot rolled to 1.5 mm thick. The hot rolled sheet was annealed at 800°C for 1 hour, air cooled, and ground to a 1 mm thickness for mechanical testing.

Tensile testing was performed on materials from all process routes and compared to AMS 4900L, AMS 4902G, and ASTM B-265. Formability testing using a Tinius Olson Ductometer was carried out on each process lot as a qualitative test comparing load and dome height at failure with that for commercial aerospace grade wrought titanium sheet that complied with both the AMS and ASTM specifications.

Compositional analysis to determine oxygen, nitrogen, and hydrogen content of the processed sheet was performed. The valuation was to determine interstitial gas contamination levels attributable to processing. An optical metallographic examination was performed on material processed by each route to compare microstructural features of consolidated material.

Property Comparison and Interpretation of Results
The test samples from all three processing routes showed properties comparable to one of the grades of titanium in either AMS or ASTM specifications, as can be seen by the test results listed in Table II. Table III shows the composition of the various sheet materials after processing. PR3 samples showed an increase in both oxygen and hydrogen during processing that was attributable to adsorbed water remnant in the steel can and on the multiple sheets prior to weld closure. Comparing the results shown in Tables II and III, tensile elongation variations can be seen to track with oxygen and nitrogen contents in the expected way i.e. higher oxygen / nitrogen levels equate to diminished elongation.

Conventional wisdom holds that tensile ductility is a good proxy for formability, however, testing of the sheet materials produced in this study proved otherwise. Table IV summarizes the formability tests, showing the dome height and load at failure for each of the three processing routes. These values are compared with those obtained from commercial wrought aerospace grade material. The powder metallurgy sheets show less formability than aerospace grade, and the formability does not track with tensile elongation. A microstructural evaluation reveals some causal factors for low formability.

Figure 2 shows a comparison of the microstructures of aerospace grade 2 wrought titanium sheet with the microstructures of the three powder metallurgy titanium sheets processed by the different routes. The grain size of PR1, PR2-A and PR3 are qualitatively similar to the aerospace grade material, however, linear defects, predominantly at grain boundaries, can be observed in PR1 material and to a lesser extent in PR3 material. As can be seen in Table II, the linear defects do not significantly reduce tensile elongation since PR1 has the highest tensile elongation of the three processing routes, yet it contains the highest fraction of visible defects. However, the defects are a likely contributor to low biaxial formability as seen in Table IV where PR1 has the lowest dome height at failure: 2.3 mm. PR2's microstructure indicates a rolled structure with no discernible grain boundary cracks. Since the microstructure of PR2 indicates characteristics of a rolled structure, the deformation likely occurred in the high alpha (<880°C) temperature range, instead of the intended beta range (> 880°C). This condition was likely caused by cold rolling mill rolls contacting the thin sheet and inducing chill during deformation. However, the microstructure shows no discernible defects and the material is fully dense.

The microstructure of PR2-A shows a typical equiaxed grain structure expected from annealing the hot rolled material at 800°C for 1 hour. No discernible microstructural defects are observed in PR2-A material and formability was the highest for any of the processing routes. A detailed understanding of the microstructural differences and subsequent mechanical property correlation is a focus of on-going work.

Identification of applications for the finished sheet and determination of the economics of the processing routes are continuing to be refined by the ORNL-led team. These efforts are directed at applications for sheet below 1 mm in thickness. Processing by methods PR2 and PR2-A requires an industrial investment in new equipment to be commercially viable, but has the advantage of potentially being a continuous process with favorable economic factors. An industrial infrastructure currently exists for methods PR1 and PR3, however, these are batch processes requiring substantial labor input. As market demand evolves, utilization of titanium powder metallurgy sheet is likely to occur first by processing routes PR1 and PR3. As industrial titanium sheet quantities increase, continuous processing via PR2 is likely to become the economic choice.

Summary

The preceding work can be summarized as follows:
1. Processing dominates the performance of roll compacted sheet
2. Properties meeting standard specifications can be achieved in sheet made from powder.
3. Uniaxial tensile testing does not predict the biaxial formability of Ti PM sheet.
4. Additional work is being performed by the team to identify optimum process routes for properties and economics.
5. Further work is ongoing to elucidate the difference in biaxial stretching response of materials produced by the different routes.

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