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Tape Casting of Porous Titanium Thin Sheets from Titanium Hydride

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ABSTRACT

Titanium thin sheets have been fabricated by tape casting using slurries based on titanium hydride powder. Titanium hydride is attractive because of its reduced cost with respect to pure titanium. Sheets of various thicknesses were tape cast, debinded, dehydrided and sintered. Porous sheets with even surfaces were obtained. Scanning electron microscopy observations of the polished cross-sections showed fine and uniformly distributed pores. Tensile strengths of up to 320 MPa have been obtained for sheets with densities close to 75% of theoretical density.

INTRODUCTION

Tape casting is a well established process for the fabrication of porous or dense thin sheets from powder [1-2]. A slurry consisting of powder, solvent, binder, plasticizer and dispersant is spread on a carrier tape. After solvent evaporation, the sheet is removed from the carrier tape, debinded and sintered to provide a solid sheet. Although more commonly used for ceramics, tape casting is also attractive for metals, in particular for the fabrication of porous structures. Metal sheets with tailored porous structures can be produced by adjusting powder characteristics and sintering conditions [2-3].

Porous titanium sheets are used as supports for catalysts, for filters and electrodes in chemical reactors and as interlayers and coatings for implants in the dental and medical industry [4-7]. Titanium is used because of its high corrosion resistance and biocompatibility. The fabrication of porous titanium sheets by tape casting from titanium powders has been demonstrated by Rak and coworkers [8]. In the present work it is shown that such sheets can also be obtained from titanium hydride powders. Titanium hydride powders are attractive because of their reduced cost compared to titanium powders [9-13].

EXPERIMENTAL

Angular TiH_2 powder from AG Materials Inc., Taiwan, was used (TIH-020A grade). The particle size distribution was determined by laser diffractometry in a Malvern Mastersizer 2000 apparatus: Dv10 = 11.18 µm, Dv50 = 20.26 µm, Dv90 = 34.94 µm, D[4,3] = 21.82 µm. The specific surface area is estimated as SSA = 6/(ρ.D[3,2]) = 0.09 m^2/g, where D[3,2] = 18.15 µm is the surface area moment mean diameter and ρ = 3.9 g/cm^3 is the density of TiH_2.

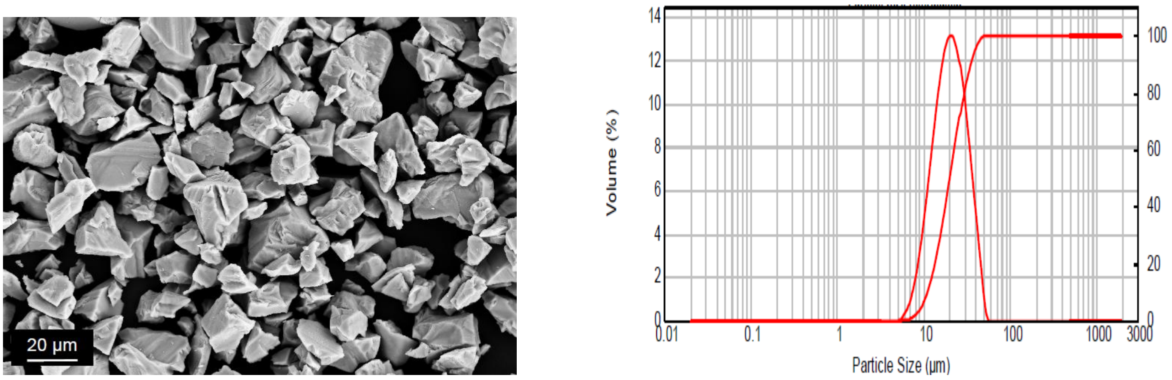
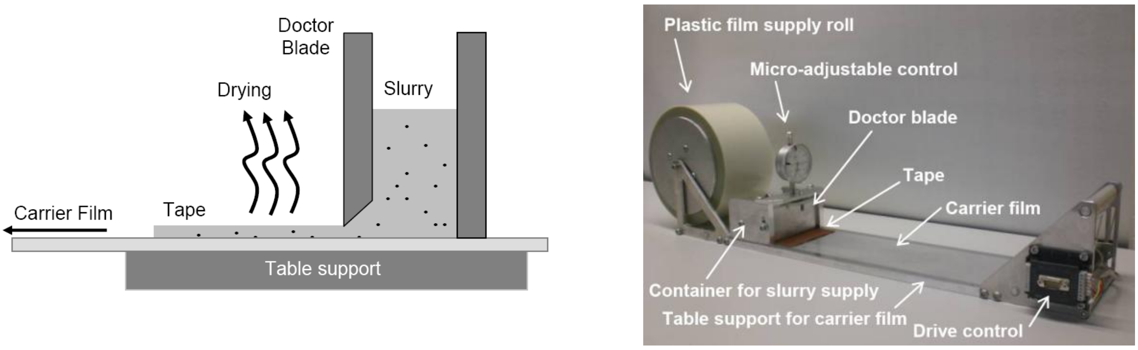


Figure 1. Scanning electron microscopy and particle size distribution of TiH_2 powder

Slurries for tape casting were prepared using the following constituents and composition:

1) TiH_2 powder, 75.0 wt%
2) Methyl Ethyl Ketone (MEK) solvent purity ≥ 99 %, 16.7 wt% (Sigma Aldrich Chemie GmbH, Buchs SG, Switzerland)
3) Ethyl Methacrylate Copolymer (EMC) B-72 binder from 6.5 wt% (R. Mistler Inc., Morrisville, PA, USA)
4) Dibuthyl Phthalate (DBP) plasticizer, purity ≥ 99 %, 1.8 wt% (R. Mistler Inc. Morrisville, PA, USA)

An acrylic binder was selected since it can be removed in the absence of oxygen [1,2] without leaving residual carbon. Wet ball mixing of the constituents was carried out in a polypropylene jar with steel balls during 4h. Green sheets were fabricated using a custom made tape-casting device (Figure 2). A silicone-coated Mylar foil was used as a carrier surface. The sheet thickness was controlled using a micro-adjustable doctor blade. The sheets were then dried until complete evaporation of solvent. After drying, the sheets were peeled off from the carrier surface and cut to the desired shape. Dried sheets, 10 cm wide, with thicknesses ranging from 0.2 mm to 1.5 mm were obtained.



(a) (b)

Figure 2. Principle of tape casting (a) and experimental set-up (b)

Green sheets were cut to rectangular specimens (Figure 3), then debinded, dehydrogenated and sintered in a Nabertherm VHT8-16MO furnace under argon atmosphere. A zirconia coated alumina support was used. The thermal cycle is shown in Figure 4. A dwell time of 1 h at 500°C was used to allow gradual hydrogen removal. Thermogravimetric analysis of TiH_2 powders performed in a Setaram TAG 24 device allowed to establish that 500°C is an appropriate temperature for dehydrogenation. Hydrogen removal proceeds during the subsequent heating to reach the sintering temperature. Sintering was performed at 1000°C for 1 h under flowing argon.

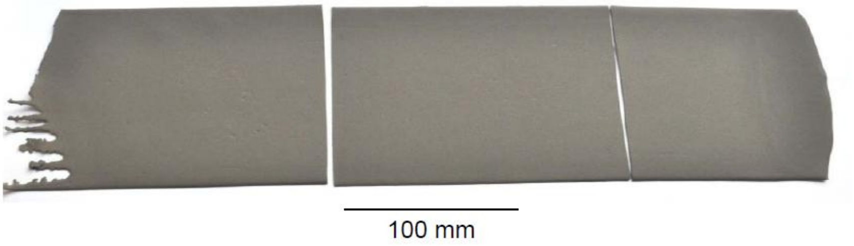


Figure 3. Tape cast green sheets

Mechanical properties were characterized by tensile tests in a Zwick 1475 machine. The samples were 5 mm wide x 100 mm long rectangular coupons machined from the sintered sheets. A gauge length of 30 mm was used. Metallographic preparation of sintered samples was performed by diamond polishing followed by oxide polishing with colloidal silica. Scanning electron microscopy was performed in a LEO 1525 microscope. Interstitial contents were measured using a LECO TCH 600 analyser.

RESULTS AND DISCUSSION

Figure 5 shows sintered tape cast sheets, from which specimens were cut for mechanical and microstructural characterization. The sheets remain flat after sintering, without significant distortion.

The shrinkage was about 18% in the cast direction, 15% in the transverse direction and 17% in thickness.

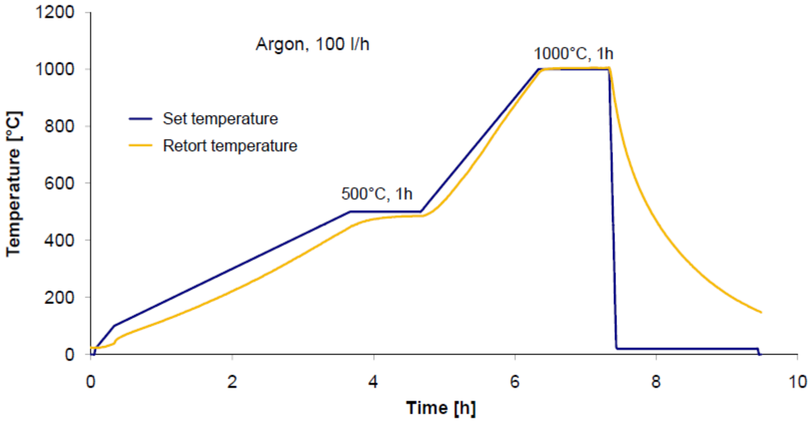


Figure 4. Thermal cycle for debinding, dehydrogenation and sintering of tape cast thin sheets

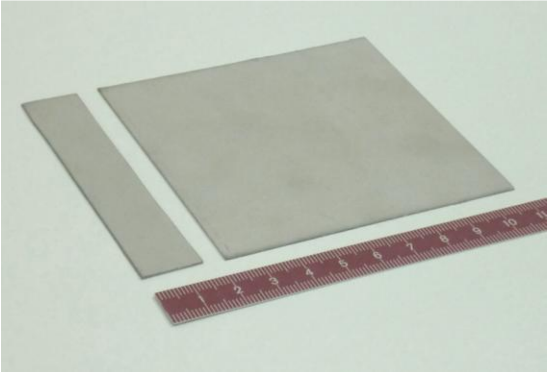
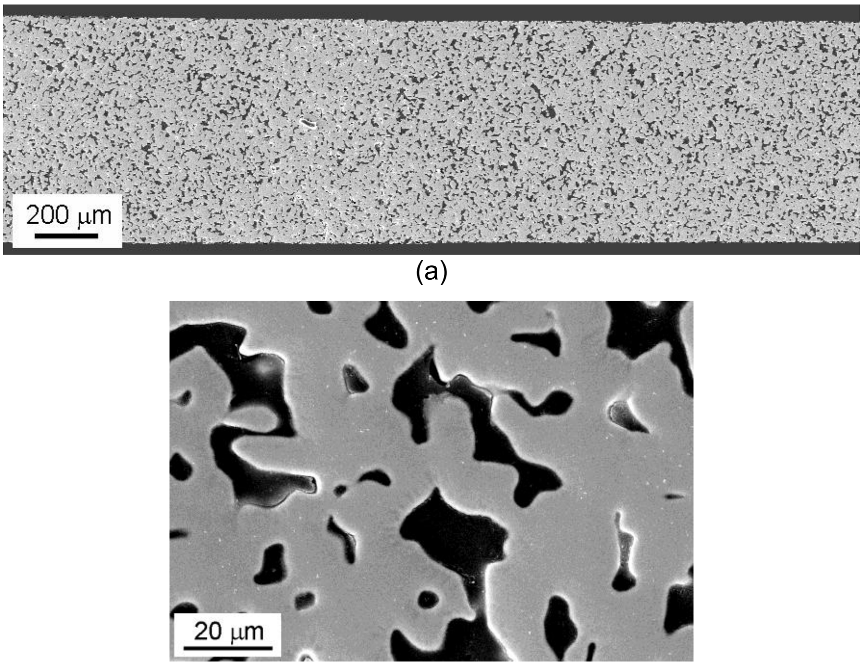


Figure 5. As sintered thin sheets of porous titanium processed by tape casting

Scanning electron microscopy observations (Figure 6) reveal a uniformly distributed porosity. The porosity was estimated as about 25 % from both geometrical and image analysis.



(a)

(b)

Figure 6. Scanning electron microscopy observations of the polished cross section of tape cast sintered titanium: full section (a), detail (b)

Figure 7 shows a typical fracture surface. The broken surface reveals a mixed fracture mode. In many areas the fracture is ductile with dimples and traces of slip observed on some fractured sintering necks. Some areas show brittle fracture.

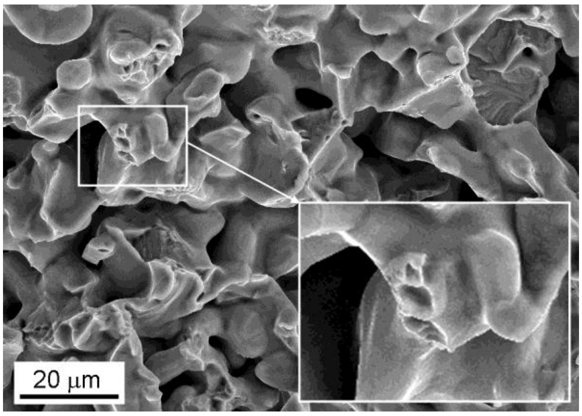


Figure 7. Scanning electron microscopy observation of the fracture surface of a tape cast sintered titanium thin sheet showing the presence of ductile dimples on a fractured sintering neck

Figure 8 shows an optical micrograph of a porous sintered titanium sheet cross section. The grain structure is made visible by the use of polarized light. The grain size is close to ASTM 7 (d_{mean}~32 µm). Some twins are visible in the grains.

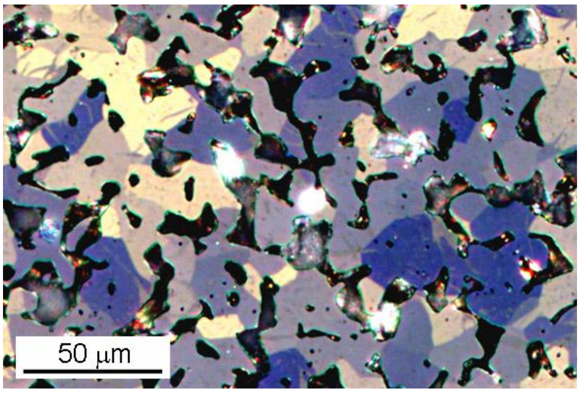


Figure 8. Optical micrograph of a polished cross section of a tape cast sintered titanium thin sheet. Black regions are pores.

Strengths in the range of 150 to 320 MPa and elongations below 1% have been measured by tensile testing. Despite the low elongation, the sheets can be deformed plastically by bending (Figure 9).

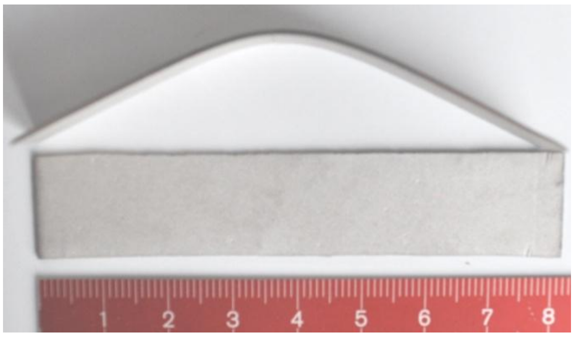


Figure 9. Tape cast porous titanium thin sheets before and after bending

Chemical measurements gave the following interstitial contents: 0.504±0.010 wt% for oxygen, 0.040±0.002 wt% for nitrogen and 0.101±0.004 wt% for hydrogen. This points out a still incomplete dehydrogenation and suggests the use of longer sintering times or higher sintering temperatures to further improve the ductility.

These preliminary results prove the feasibility of obtaining porous titanium sheets from TiH_2 powder, a development which is in progress.

CONCLUSIONS

The feasibility of producing titanium sheets by tape casting from titanium hydride powders is assessed. The sheets exhibit a uniform porous microstructure. The porosity is about 25%. The sheets can be plastically deformed by bending. Strengths in the range of 150 to 320 MPa have been measured by tensile tests. Titanium hydride powder is a good candidate as base material because of its reduced cost compared to pure titanium powder.

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