Presentation

NANO-REINFORCED TITANIUM COMPOSITES AS CANDIDATE PRESSURE VESSEL MATERIALS FOR DEEP ATMOSPHERIC PROBES

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ABSTRACT

Probes to Venus and the gas giants are generally composed of a heat shield protecting a spherical titanium pressure vessel. Once the high-speed entry portion of the entry is completed, the heat shield may be ejected (as was the case with Pioneer Venus) and the titanium vessel, housing the scientific instruments, is exposed to perform in-situ atmospheric measurements. The effort reported here is focused on evaluating property enhancements due to additions of nano-reinforcements to the titanium base material. Initial modeling reported at the 2004 Probe Workshop, has suggested that the addition of a nano-reinforcement phase to the baseline titanium system could provide decreased density and thermal conductivity and increased modulus, an indication that development of such composite materials would be valuable.

The pressure vessel structure is a mass driver for the probe, and the mass reduction enabled by such properties in the nano-reinforced material would allow a greater science payload. The overall objective of this work is to develop a candidate material to allow deep probe pressure vessels of reduced mass.

Two methods of consolidating materials were evaluated in this study. In the first method, samples are consolidated using free sintering and in the second case samples are consolidated using spark plasma sintering. Microstructure and material properties of titanium and titanium matrix particulate composites, consolidated by both approaches, have been investigated. Materials characterization, including hardness, modulus, X-Ray Diffraction and scanning electron microscopy help in defining the advantages of the spark plasma sintering consolidation method over conventional free-sintering. Titanium composite samples consolidated by spark plasma sintering yield lower density materials, and preliminary properties indicate superior mechanical performance.

BACKGROUND

The extremely harsh environments to which probes are exposed during entry and descent into a planet's atmosphere dictate planetary probe design [1]. The Pioneer Venus probes, for example, were travelling at approximately 11.7 km/s when they first entered the Venus atmosphere. For each probe, after sufficient slowing the deceleration module is ejected and the probe exposed to the atmosphere. During further descent the probes encountered sulphuric acid clouds. With descent, each probe experienced substantial increases in both pressure and temperature. Towards the end of their mission the surface temperatures of the probes were approaching 400°C and they were exposed to external pressures of 100 atm. The probe pressure vessel must withstand these severe conditions and protect the science payload.

Titanium has been the material of choice for the pressure vessel portion of past probe missions, such as Pioneer Venus [2]. Desirable properties of Ti - high specific strength, high strength retained at high temperatures (up to 550°C) and superior corrosion resistance in most natural environments - make it a candidate material for many applications. The main drawback of the material is its cost. Nevertheless, for space applications where high specific strength and superior strength retention to higher temperatures are critical, Ti is the primary candidate.

We are currently evaluating the potential of replacing titanium with a nano-reinforced titanium matrix composite. The advantages of particulate-reinforced Ti metal matrix composites include reduced mass and improved performance (increased strength and modulus) over the base metal. However, the disadvantage of hard reinforcement phases in a ductile matrix is a marked loss in toughness. This loss can be mitigated if the particles are small enough and well

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dispersed. By carefully controlling the volume fraction of reinforcement, and using novel processing approaches, it is possible to process nano-reinforced components with a refined grain structure.

A breakdown of the mass of the Pioneer Venus probes consumed by the titanium pressure vessel is presented in Table 1[1]. For both the large and small probes, approximately one third of the total probe mass was tied to the pressure vessel. From Table 1 it is apparent that the pressure vessel is a mass driver for the probes, and any reduction in pressure vessel mass could lead to increased science payload. The replacement of titanium with a titanium matrix composite offers the possibility of mass reduction in probe pressure vessel design.

Table 1: Breakdown of pressure vessel components by mass (taken from Ref [1])

Probe	Pressure Vessel Mass (kg)	Total Probe Mass (kg) (not inc. decel. module)	Science Instrum-entation Mass (kg)	Pressure Vessel Structure Mass Fraction (%)
Pioneer Venus Large Probe	62	193	35	32
Pioneer Venus Small Probe	18	61	5	30

The key to superior performance in metal matrix composites is uniform distribution of particles throughout the matrix. For example, initial studies at NASA GRC [3] have indicated that Ti matrix composites with 10 wt. % TiC offer a technology with promise to lower the cost and weight of space-access propulsion systems. At the evaluated TiC loading (10%), the composite retained excellent machinability. Tensile and low-cycle fatigue testing was conducted and it was observed that the stiffness of the composite was increased by 19% over the baseline metal when tested at 427 °C. The yield strength and tensile strength of the composite were 23% and 14% greater respectively than the baseline Ti alloy. The composite's increased strength however, is offset by a 20% reduction in ductility and a 33% reduction in fatigue life, as the brittle TiC particulates act as stress risers in the Ti matrix. A spark plasma sintering consolidation approach used in this work is expected to yield materials with an improved ductility that is due to the very fine microstructure formed in SPS consolidation, and to the likliehood that they are coherent with the matrix (not the case with the materials in Ref [3]).

A theoretical study presented at the 2004 Probe Workshop highlighted the potential benefits of titanium matrix composites with nanotube- or fullerene-additions for pressure vessel materials in deep space probes [4]. This study showed that such composite systems offer improved thermal and mechanical performance over baseline Ti systems, allowing the possibility of a reduced mass pressure vessel.

EXPERIMENTAL APPROACH

Titanium powder obtained from AEE (99.7% purity and average particle size of 20 microns) was used to process both the titanium and titanium matrix composites. Single-wall nanotubes used in this study were obtained from BuckyUSA and fullurenes were obtained from Nanolabs Inc. A uniaxial press was used to form samples with varying amounts of reinforcements (<30%). This process was followed by cold isostatic pressing at 30ksi, to yield high density green compacts. These compacts were consolidated by both conventional free sintering and spark plasma sintering (SPS). Compacts consolidated via free sintering were fired at temperatures ranging from 1150°C to 1550°C, in a tube furnace with an alumina tube and a flowing argon atmosphere. Samples processed by SPS were consolidated at 600°C.

Spark Plasma Sintering

SPS is a recently developed rapid sintering process [5]. This process leads to densification at much lower temperatures than conventional consolidation allows and yields materials with very fine grained microstructures. In SPS both a low voltage, high density pulse current and uniaxial pressure are applied during consolidation. A pulsed direct current is passed through the graphite die (and, in this case, also through the sample, since titanium is electrically conducting). A schematic of the SPS process is given in Fig. 1. The main advantages of this method include rapid heating of the sample, short hold times at temperature, rapid cooling and low sintering temperature. To date, the effect of various SPS variables, such as pulse time and total current, on the microstructure of the

processed material is not clearly defined. Research is ongoing in this field.

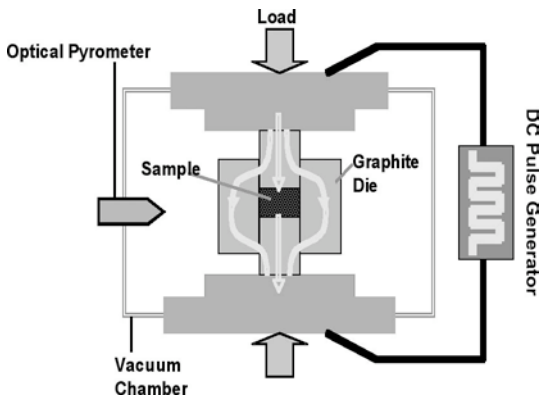

Fig. 1: Schematic of SPS Approach

Characterization

Density and open porosity of compacted samples was obtained using Archimedes approach. Micrographs of consolidated samples were obtained by optical microscopy (Zeiss). Prior to imaging, all samples were ground and polished to a 0.25 micron finish with diamond grinding media. Samples were then etched by immersion in a solution of water, KOH and H_2O_2.

Throughout this work X-Ray Diffraction (XRD) (Thermosciences X-Ray Diffractometer) was used to characterize phase evolution, crystallinity and purity. The radiation source was Cu-Kα (45kV and 40mA) and scans were taken between 2θ of 10° and 90°, with a step width of 0.02 degrees. Solid samples were polished to a 1 μm finish prior to XRD scan. JADE software was used to analyze all XRD scans and to identify phases.

A hardness tester (Schimadzu HSV-30)) with a Vickers indenter was used to determine hardness as a function of load. The values presented here are an average of 3 measurements obtained at each load. Prior to loading, all samples were polished to a 1 micron finish.

The Young's Modulus was determined by a pulse echo technique. In this technique, the resonant frequency of the material is determined and then Eq. 1 is used to obtain modulus.

$$E = CMf^2 \qquad (1)$$

where C is a constant determined from specimen shape size and poisson's ratio, M is the sample mass and f is the frequency of vibration. This approach can be used to determine flexural, longitudinal and torsional moduli.

RESULTS

Density

The remaining discussion will be limited to three samples: a titanium sample processed by free sintering, and a titanium sample and titanium matrix composite sample processed by SPS. The densities and residual porosity after consolidation for these three samples are summarized in Table 2. It is apparent that SPS yields almost fully dense materials at very low processing temperatures, and offers a very promising processing route to allow the production of dense materials with very fine microstructures. Free-sintered titanium did not reach full density at 1550°C. The theoretical density of titanium is ~4.5g/cc.

Table 2: Density and Porosity Data for Select Samples

Sample	Processing	Density (g/cc)	% Residual Open Porosity
Ti	Free sintering in Ar to 1550°C	4.1	5.1
Ti	SPS at 600°C	4.49	0
Ti – 20vol% SWNTs	SPS at 600°C	4.01	2.89

Microstructure

Micrographs of titanium processed by free sintering to a maximum temperature of 1550°C and processed by SPS with a maximum temperature of 600°C are presented in Figs. 2 and 3 respectively. These micrographs demonstrate that microstructures of the titanium vary significantly as a result of different processing routes. This observation also holds for titanium matrix composites, where similar trends were observed. Titanium undergoes a phase change at 882°C in which α titanium transforms to the β phase. Systems that are annealed or slowly cooled will have a stable microstructure with large equiaxed grains, as in Fig. 2. Systems that are rapidly

quenched during the processing step may form metastable phases that contain Widmanstatten plated, or display an acicular structure [6]. The rapid cooling of the SPS consolidated titanium shown in Fig. 3 yields acicular _ grains with a very refined microstructure. This microstructure is unique in that the processing temperature may not have exceeded the phase transition temperature during consolidation.

A representative micrograph of an SPS consolidated nano-reinforced titanium composite is given in Fig. 4. This composite was also processed at 600°C, with a short hold time at temperature. This composite contained 20 vol% single wall nanotubes (SWNT). While the microstructure is fine grained, it is non-uniform in nature and contains rather large agglomerates which are due to the non-uniform dispersion of the nanotubes during processing. It is easier to achieve more uniform microstructures in nano-reinforced titanium matrix systems with SWNT loadings less than 5 vol%.

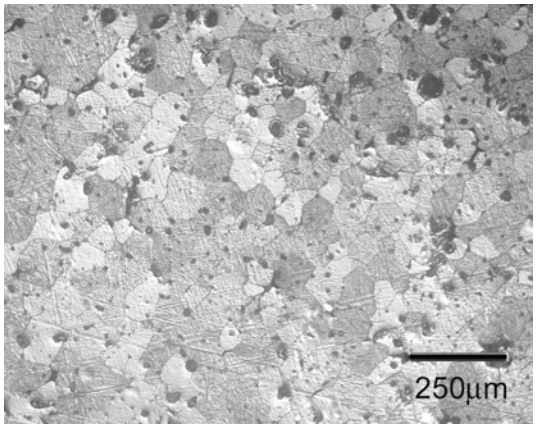

Fig. 2: Micrograph of titanium free-sintered at 1550°C in argon

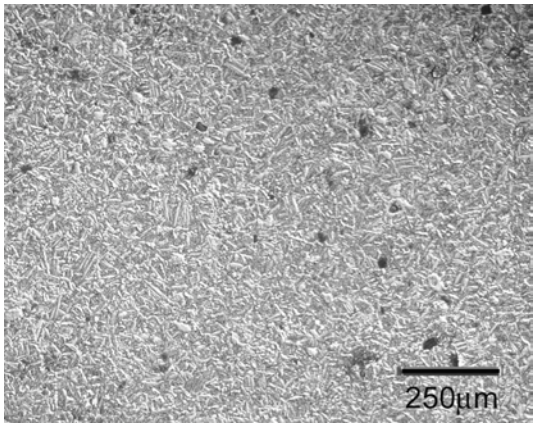

Fig. 3: Micrograph of titanium consolidated by SPS at 600°C in argon

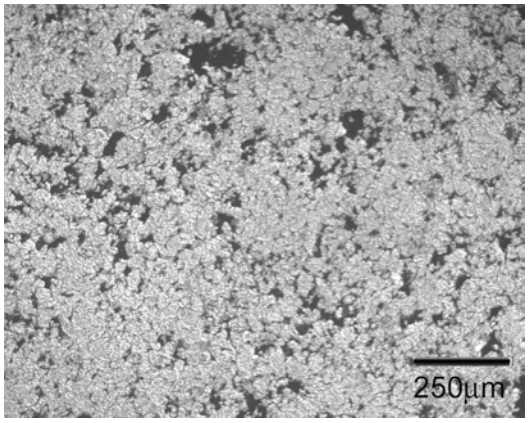

Fig. 4: Micrograph of titanium with 20 vol % SWNTs consolidated by SPS at 600°C in argon

Phase Evolution

Fig. 5 displays the patterns for samples processed both by free sintering and SPS. The free-sintered sample was consolidated at 1150°C and the SPS sample was consolidated at 600°C. Both have three titanium peaks, at approximately 35°, 38° and 40°, which correspond to the α titanium phase which is stable at room temperature. It is also noted that the SPS processed composite sample formed some TiC even when processed at 600°C with a short processing time. The extent of reaction of the SWNT phases is currently being investigated by transmission electron microscopy. Complete conversion of the carbon reinforcement phase is expected in all samples processed by free sintering. Retention of some of the carbon phase, however, in samples processed by SPS, and the accompanying fine-grained microstructure are likely to have mechanical properties desirable for a pressure vessel.

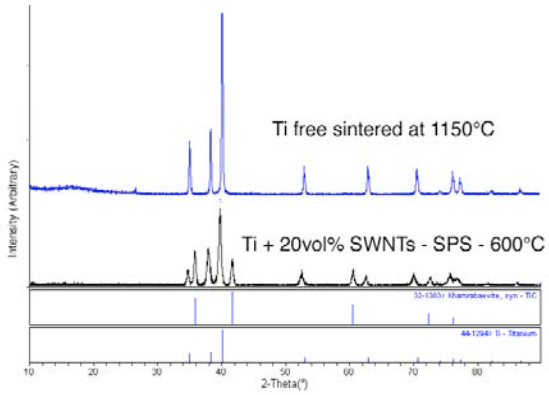

Fig. 5: Phase evolution of titanium with 20 vol % SWNTs consolidated with SPS at 600°C in argon, and a titanium sample free-sintered at 1150°C

Modulus

Modulus values have been obtained for two samples: a titanium sample and a titanium composite with 20 vol% SWNT loading, both processed by SPS. A modulus of 117 GPa was obtained for the titanium sample, which corresponds very well with the literature value of 116 GPa for pure titanium. A modulus of 280 GPa was obtained for the titanium composite. It has yet to be determined what portion of the SWNTs in this composite has reacted with the titanium matrix during processing. As a result, it is difficult to predict the modulus from available empirical models. Nevertheless, these preliminary results indicate advantages to adding nano-reinforcements to the Ti matrix.

Hardness Measurements

Hardness values at varying loads are plotted in Fig. 6 for three samples: a free-sintered titanium material sintered at 1550°C, a titanium and a titanium composite (with 20 vol% SWNTs), both processed by SPS at 600°C. The free-sintered titanium sample has a substantially higher hardness value than either the titanium or titanium composite samples processed using SPS. The increased hardness in the free-sintered sample may be explained by oxygen contamination. The free-sintered samples are more prone to oxidation because of the higher firing temperatures and longer times. Contamination with small amounts of oxygen impurities from the processing step move to interstitial sites in the titanium crystalline lattice and have been shown experimentally to increase hardness [7]. These contaminants are deleterious if a material of high toughness is desired, as they impede the movement of dislocations, which reduce ductility and toughness in the material. However, the hardness and strength of the material are improved with increased interstitials. Pure titanium is an α phase alloy, in which the amount of oxygen dictates the strength. Commercially, oxygen is added to pure titanium to increase its strength. It is noted that the SPS processing route results in less contamination.

The titanium composite has an uncharacteristically low hardness, considering that this material had a substantially higher modulus that the pure titanium material. The lower-than-expected hardness is likely due to the residual porosity (~2.9%) in the material. Moreover, samples processed by SPS have a greater percentage of grain boundary phases and nanocrystalline reinforcements which, in themselves may also contribute to lower hardness values. Further use of SPS to optimize the consolidation of the composite systems is currently ongoing.

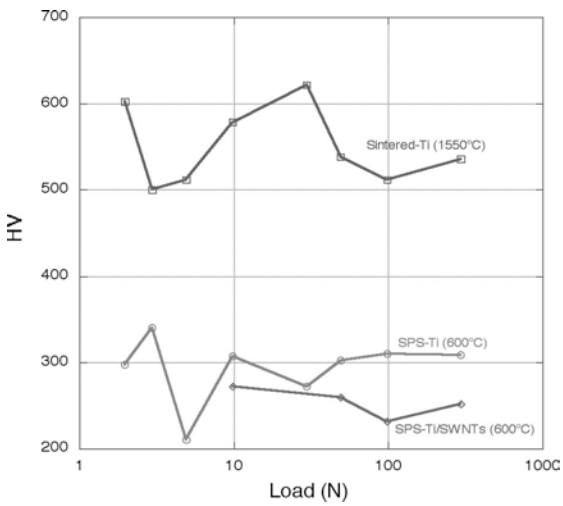

Fig. 6: Hardness values for free-sintered titanium sintered at 1550°C, titanium processed by SPS at 600°C and a titanium composite processed by SPS (with 20 vol% SWNTs). Hardness values were obtained at different loads

Images of the Vickers indentations produced at the highest load (294N) on the free-sintered titanium sample, the titanium sample processed by SPS and the titanium composite (with 20 vol% SWNTs) are presented in Figs. 7, 8 and 9 respectively. Brittle behaviour is observed in the free-sintered sample, as cracks are observed to emanate from the indent corners, as evident in Fig. 7. This brittle behaviour can again be attributed to oxygen contamination during the free sintering step. Both the titanium and the titanium matrix composite processed by SPS display ductile behavior with plastic flow evident

around the indentation area. The indentation behavior for the titanium composite is very encouraging, since a substantial amount of TiC is present in the material. TiC is a very brittle, high strength material, but the refined nature of the composite microstructure may account for the non-brittle indentation in Fig. 9. Further work is needed to better understand the hardness values and ductile behavior in the titanium composites processed by SPS.

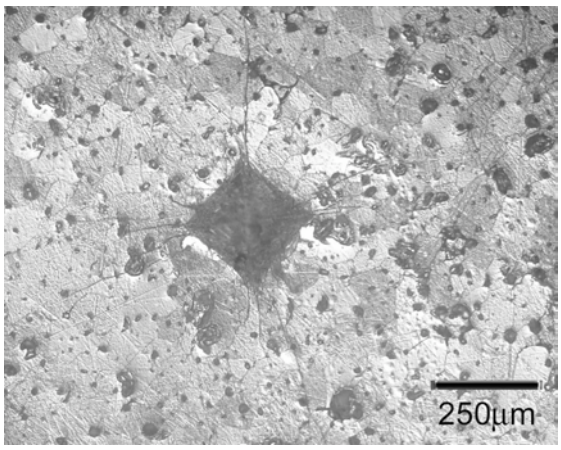

Fig. 7: Vickers indentation on a free-sintered titanium (sintered at 1550°C)

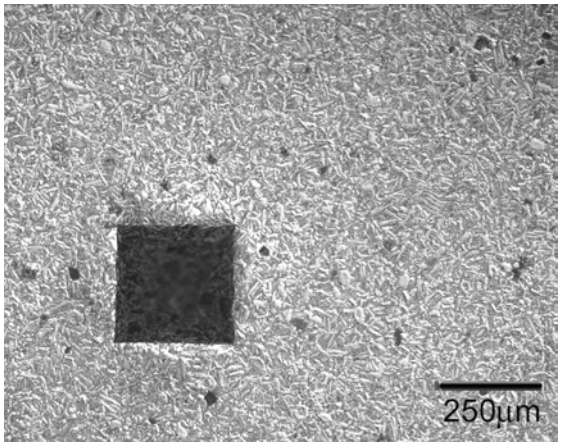

Fig. 8: Vickers indentation on an SPS consolidated titanium sample (consolidated at 600°C)

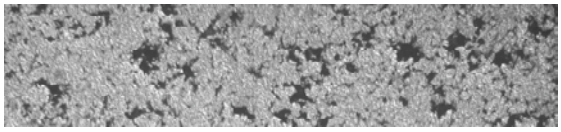

Fig. 9: Vickers indentation on an SPS consolidated titanium composite sample (with 20 vol% SWNTs consolidated at 600°C)

SUMMARY

The current study is evaluating the potential of a nano-reinforced Ti composite as a structural material for probe pressure vessels. Initial modeling has indicated that the addition of a nano-reinforcement phase could provide decreased density and increased mechanical performance over the baseline Ti system, thereby offering a lower-mass material for pressure vessels. The pressure vessel structure is a mass driver for the probe, and the mass reduction enabled by such properties in the nano-reinforced material would allow a greater science payload. To date, free-sintered and SPS samples have been processed, and preliminary properties compared. SPS provides an attractive rapid processing route, allowing retention of the fine-grained structure in both titanium and titanium composites. The process consolidates samples at much lower temperatures than conventional processing routes. Preliminary hardness data indicate that samples processed by SPS have superior toughness than free-sintered samples. This may be due to less O_2 contamination in the SPS processing route and to the fine-grained microstructure obtained with this consolidation technique. Complete reaction of the carbon reinforcements with the Ti matrix is observed in free sintering. Current TEM studies are being undertaken to determine the extent of reaction of the reinforcement phase in SPS processed composites.

Initial composite samples processed by SPS have a ~10% mass reduction over the baseline titanium. Preliminary mechanical properties (modulus) also show improvement over the basline titanium (>200%). Initial results indicate that this approach offers a potential lower-mass alternative for

pressure vessel materials. This research effort will support the development of a fundamental understanding of titanium matrix composites processed by SPS.

FUTURE WORK

Future efforts will focus on further optimizing the processing of nano-reinforced titanium matrix composites by SPS. A TEM study is in process, to determine if the reinforcements are coherent with the titanium matrix of composites processed by SPS. Once better processing optimization has been achieved, the mechanical properties of the titanium composite materials will be evaluated.

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