Nano-Reinforced Ti Composites as Candidate Pressure Vessel Materials for Deep Atmospheric Probes

M. Stackpoole[(1)], D. Srivastava[(2)], A. Fuentes[(3)], B. Cruden[(2)] and J.O. Arnold[(2)]

[(1)]ELORET Corp., Sunnyvale, CA 94086, USA
[(2)] NASA Ames Center for Nanotechnology, Moffett Field, CA 94035, USA
[(3)] University of Texas, Pan American, USA

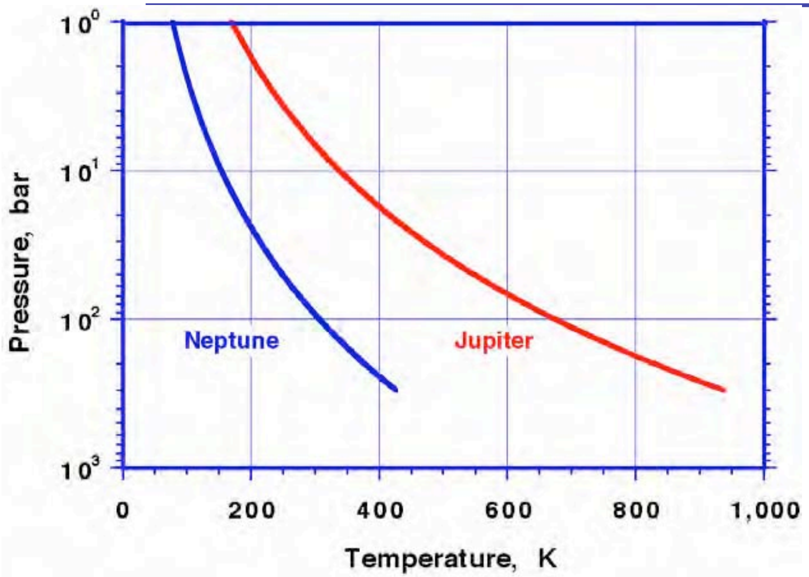
Funding provided by IR&D and NASA Ames

3rd International Planetary Probe Workshop, June 25 - July 1, 2005

Outline

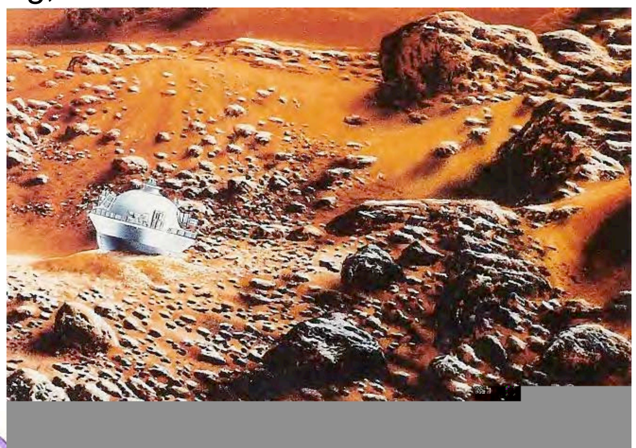
- Background
  - Material Challenges for Deep Space Probe Design
  - Possible benefits of Nano-Reinforced Ti Composites for Pressure Vessels
- Research Goals
- Experimental Approach
  - Processing Outline
  - Spark Plasma Sintering (SPS)
  - Microstructure
  - Modulus Data
  - Phase Evolution
  - Hardness Data
- Conclusions and Future Work

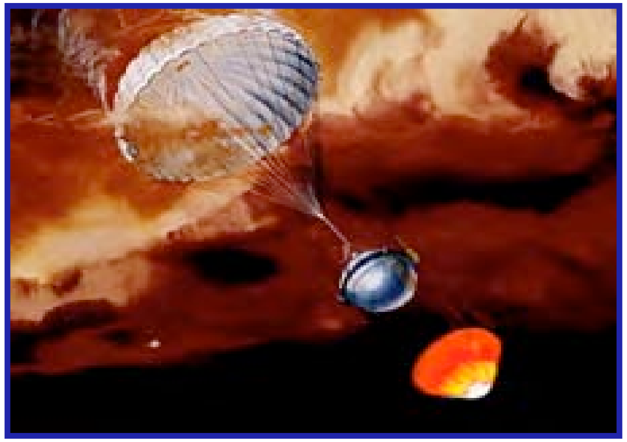
Material Challenges for Deep Space Probes



Atmospheric profile provided by Rich Young, NASA ARC

•A significant challenge in deep space probe design is to have a pressure vessel material
- able to withstand the extremely harsh environments experienced during descent into the planet's atmosphere or on its surface
- able to yield an acceptable mass fraction





Artist's Concepts of Pioneer-Venus, Small "Day" Probe

Pressure Vessel Material for Pioneer-Venus Mission

- Harsh entry environment for probe at Venus
  - Probe velocity ~ 11.7km/sec at start of entry
  - Deceleration during entry phase in excess of 300gs
  - Sulphuric acid present in atmosphere
  - Large increase in ambient temperature and pressure
    - Temperatures of ~400°C and pressures of 100atm
- Titanium selected as pressure vessel material for Pioneer Venus missions
  - Ti has excellent corrosion resistance
  - Ti has good strength retention at high temperature

Pressure Vessel Structure Mass Fraction

Probe	Pressure Vessel Mass (kg)	Total* Probe Mass (kg)	Science Instrumentation Mass (kg)
Pioneer Venus Large Probe	62	193	35
Pioneer Venus Small Probe	18	61	5

- Pressure vessel structure a mass driver for the probe
  - Reduction in mass makes possible increased science payload

Source: B. Bienstock Proceedings from Planetary Probe Workshop 2003 (ESA SP 544, Feb 2004)

* Excludes deceleration module mass

Potential Benefits of Nano-Reinforced Ti Composites for Pressure Vessels

- Nano-reinforced titanium may lead to a reduction in pressure vessel mass
  - **Lower density** than Ti
  - **Higher specific modulus** than Ti and **higher specific strength** than Ti
    - **Increased strength and stiffness** from hard reinforcement particulates or short fibers added to ductile Ti matrix
    - These phases *generally* have a detrimental effect on toughness
      - May be mitigated if the particles are **small enough** and well dispersed

Goals of Current Research

Develop a candidate material to allow deep probe pressure vessels of reduced mass

Specific goals:

- Determine if nano-reinforcement phases can be achieved by additions of fullerenes (C-60) and nanotubes (SWNTs) to Ti composites
  - Investigate if the reinforcement structure is retained at the same scale after consolidation
- Investigate what reinforcement phases are present (reactive processing route)
- Investigate effect of reinforcements on properties

Outline of Processing Route

Characterization of Starting Constituents

- SEM micrographs
- Particle size distribution
- X-ray diffraction

→

Milling / Mixing

- Particle size reduction
- Additives: dispersants, binders & solvents
- Dry route vs. slurry route

→

Consolidation

- Free sintering
- SPS
- Hot-pressing

↓

Processing Parameters

- Time
- Temperature
- Pressure
- Atmosphere

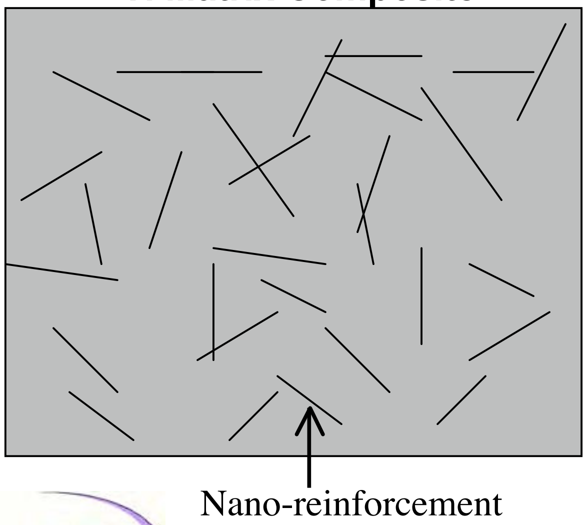
←

Characterization of Consolidated Materials

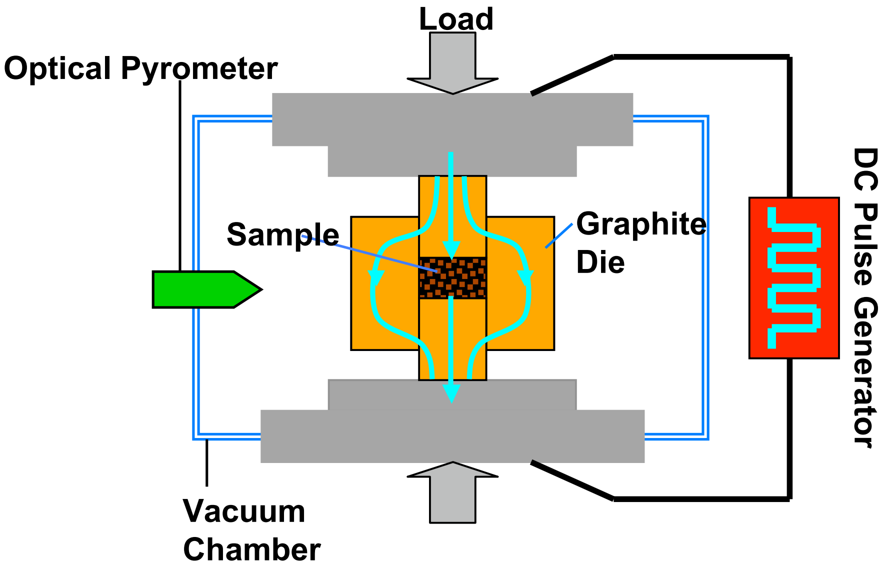
- SEM or optical micrographs
- Modulus
- Hardness
- Phase Evolution
- TEM
- Thermal Conductivity
- Mechanical Properties
- Corrosion Resistance

←

Schematic of Nano-Reinforced Ti Matrix Composite

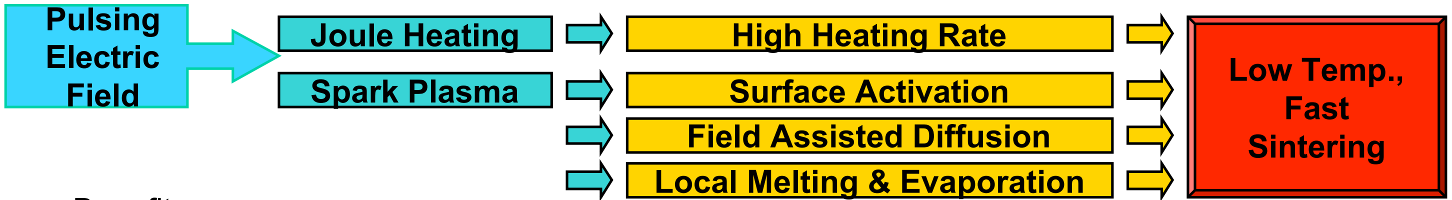


Spark Plasma Sintering (SPS)



Factors contributing to fast densification include:

- High heating rate
- External pressure
- Fast cooling



Benefits:

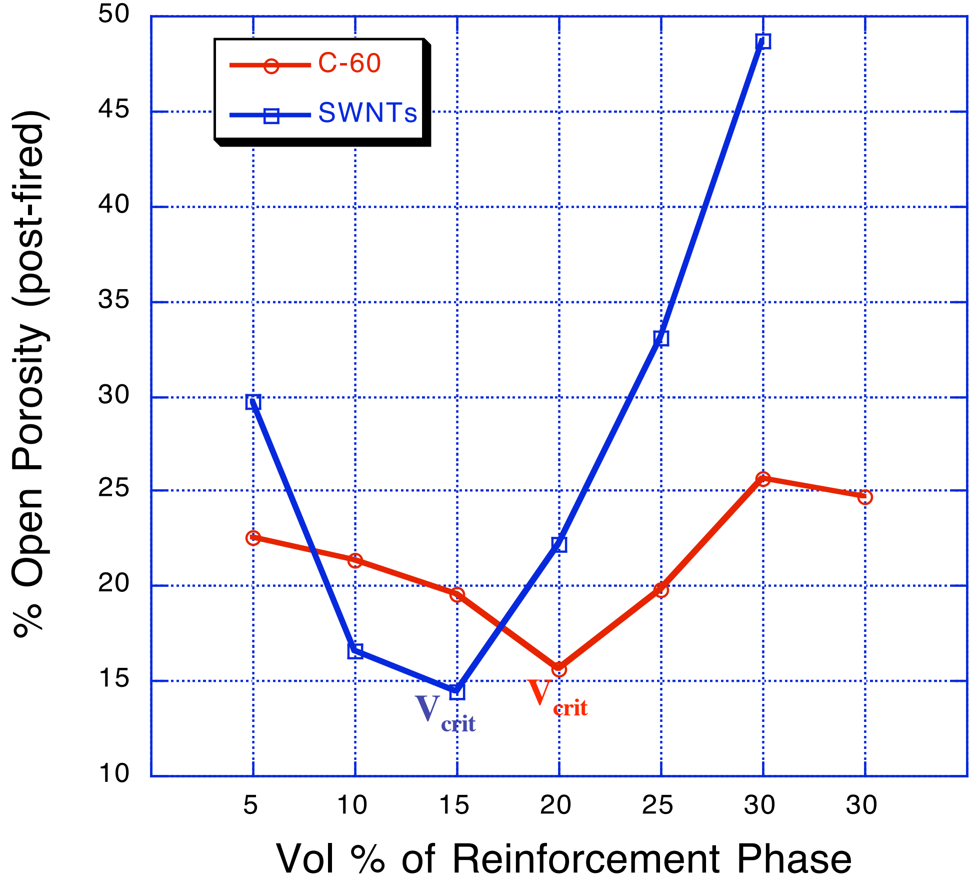
- Low processing temperatures compared to conventional processing routes
- Fast heating and cooling rates, short holding times (limits grain growth)
- Enable processing nano-grained parts

Limitations:

- Scale-up is a concern
- Currently SPS applies only to axi-symmetric sample geometry

Effect of Reinforcement Geometry and Volume Fraction on Consolidation

Effect of reinforcement loading

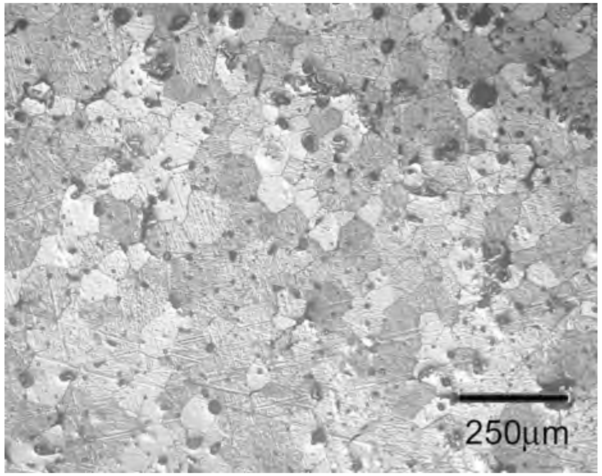


- Spherical reinforcements have a higher packing density than high-aspect-ratio reinforcements
- Critical filler volume (V_{crit})* **lower** for high-aspect-ratio fillers
- At loadings above V_{crit}, filler particles will touch one another and form a non-deformable network, inhibiting further densification by free sintering
- Results shown here for free sintered cases only (1150°C)

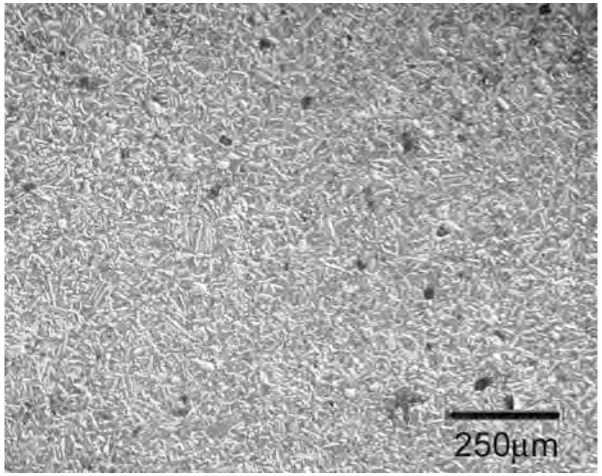
*Filler content required to form a rigid network and prevent densification of the Ti matrix

Microstructural Features of Ti and Ti Composite

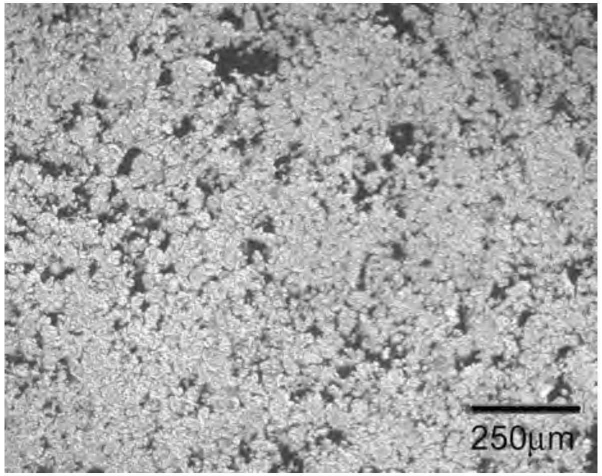
Ti Free Sintered at 1550°C



Ti SPSed at 600°C

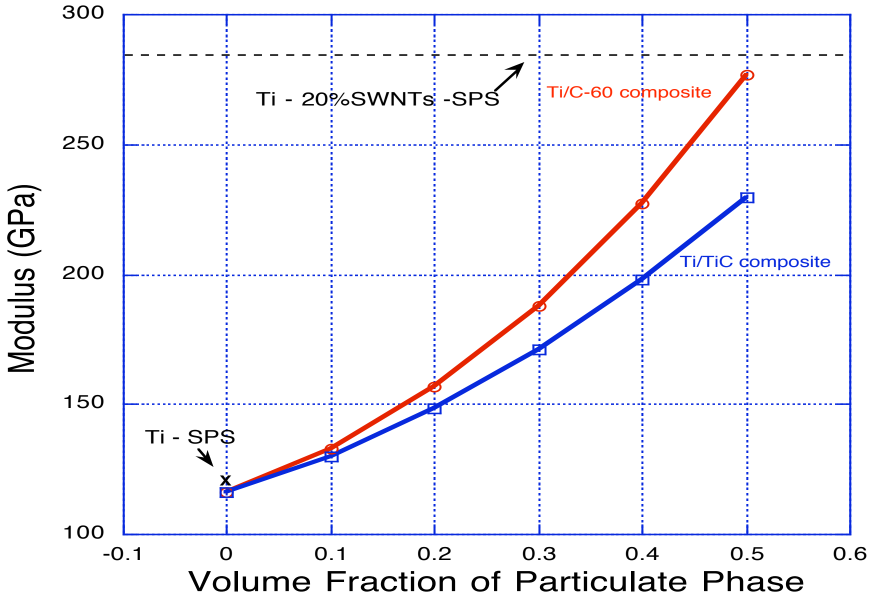


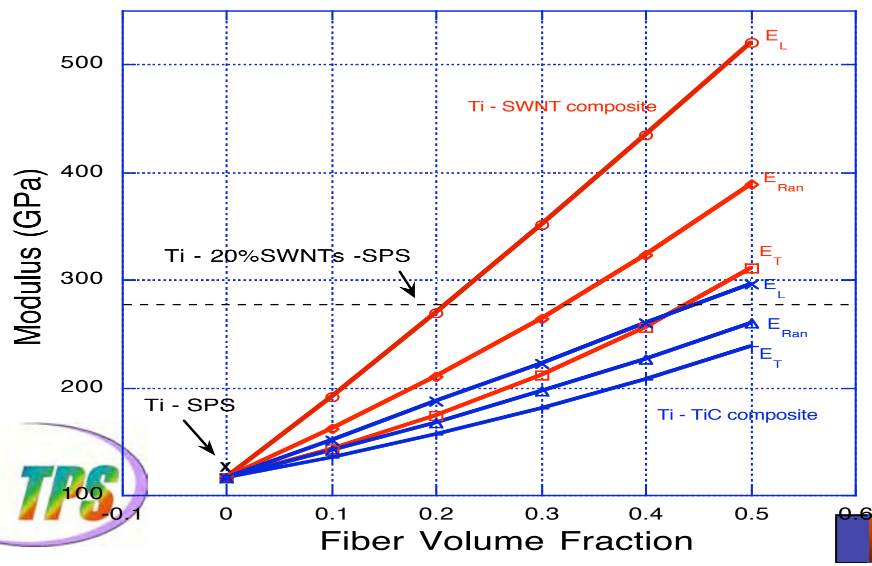
Ti/SWNTs SPSed at 600°C



- The slow cooling of the free sintered Ti gives equiaxed _ grains that may contain β spheroids
- The rapid cooling of the SPS consolidated Ti yields acicular _ grains with a very fine microstructure
- A non-uniform microstructure is observed in the Ti composite samples
  - Possibly due to high SWNT loading

Modulus of Ti and Ti Composites





Particulate Composite Case*

(Assume Ep = 860GPa and Em = 116GPa)

$$E_{pc} = \frac{V_f^{0.67} E_m}{1 - V_f^{0.33}\left(1 - \frac{E_m}{E_f}\right)} + (1 - V_f^{0.67}) E_m$$

Modulus of Ti-20%SWNT starting materials higher than model predicts

*Mittal et.al., NASA Technical Report, 1996

Short Fiber Composite Case**

(Assume l/d = 20, Ef = 1000GPa and Em = 116GPa)

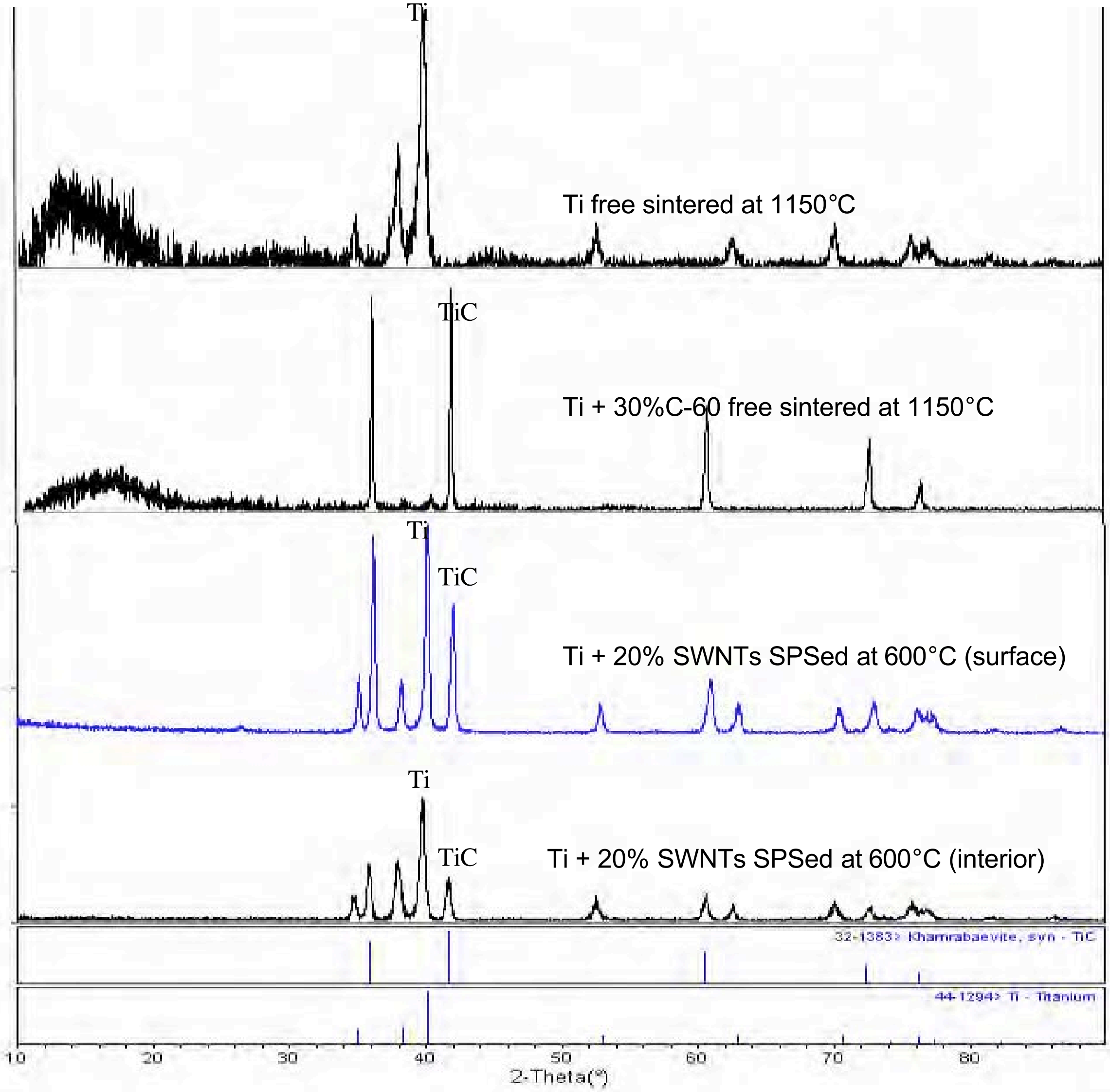
$$\frac{E}{E_m} = \frac{1 + \xi \eta V_f}{1 - \eta V_f} \qquad \eta = \frac{(E_f / E_m) - 1}{(E_f / E_m) + \xi}$$

ξ = 2l/d for longitudinal and 2 for transverse modes

Modulus of Ti-20%SWNT starting materials falls within model prediction range

**Halpin-Tsai Eqns from Agarwal & Broutman, Wiley Intersciences, 1990

Phase Evolution in Ti and Ti Composites

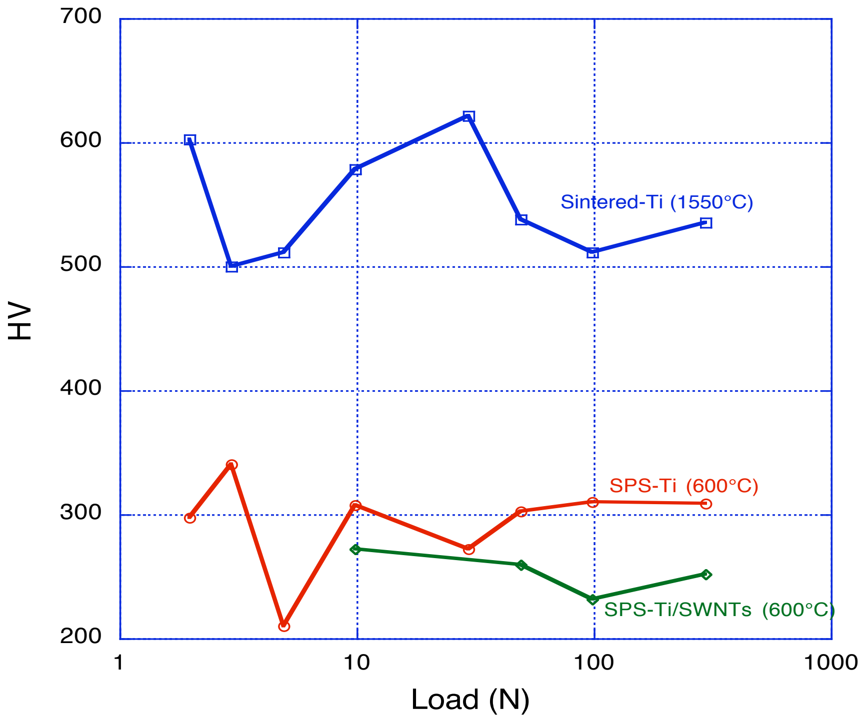


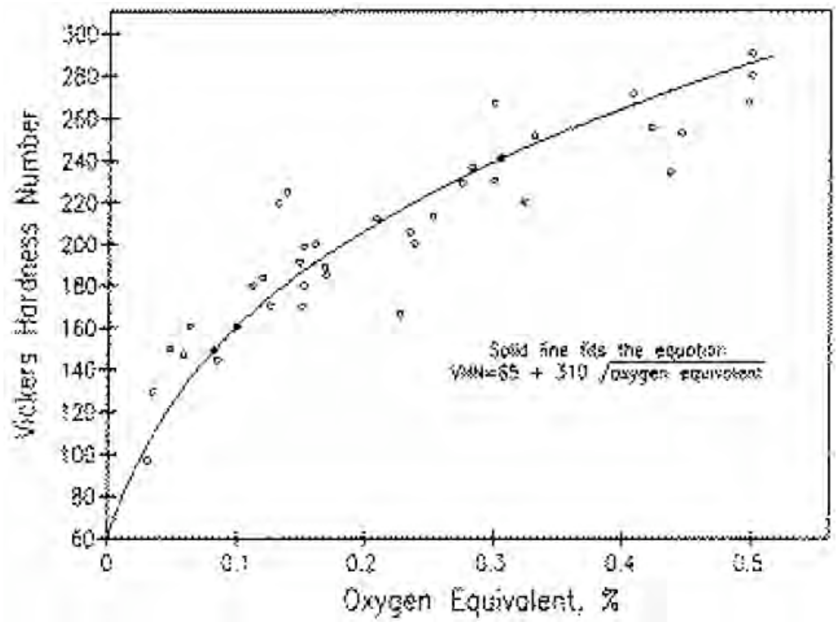
Higher processing temperaturesand longer processing times of free sintered approach makes formation of TiC more likely

Formation of TiC may not have gone to completion in SPS processed samples

Completeness of particulate formation to be determined with TEM

Hardness Data for Ti and Ti Composite



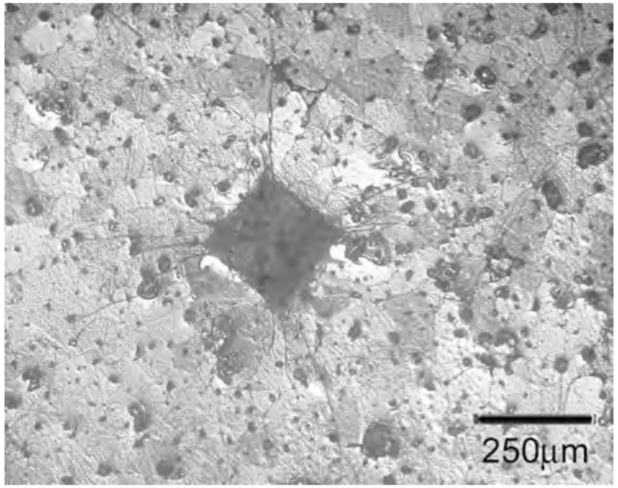


Source: Ogden and Jaffee, Battelle Memorial Institute. TML Report # 20, 1955

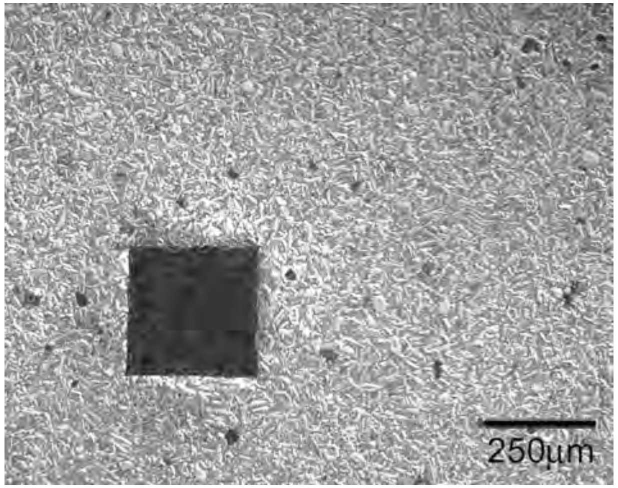
- Interstitial content (due to oxygen contamination) has a large influence on hardness
  - SPS results in less oxygen contamination
- Effect more pronounced in free sintered samples

Hardness Data for Ti and Ti Composite

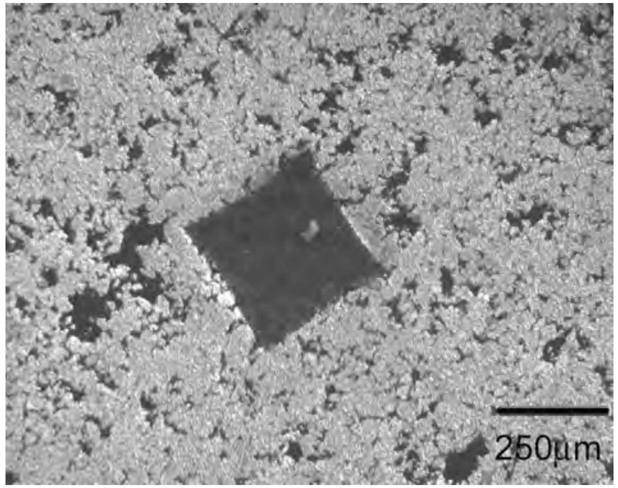
Ti Free Sintered at 1550°C



Ti SPSed at 600°C



Ti/SWNTs SPSed at 600°C



- Brittle fracture observed in the free sintered Ti sample
  - Due to oxygen contamination
- Both Ti and Ti/SWNT SPSed samples display ductile behavior
  - Plastic flow observed around the indentation area
  - Indicates material of higher toughness

Load ~ 400N

Conclusions and Future Work

Conclusions

- **Samples processed to date indicate that this approach offers a potential lower mass alternative for pressure vessel materials**
  - **Lower Density in SPS composites (~ 10% mass reduction)**
  - **Higher specific modulus (>200%)**
  - Higher specific strength (in progress)
  - Lower thermal conductivity

- Ti and nano-reinforced Ti composites consolidated by free sintering and SPS indicate
  - SPS provides an attractive processing route, allowing retention of the fine grained structure in Ti composites
  - Scale of reinforcement phase should also be retained at a refined level

Future Work

- TEM to determine composition of reinforcement phases
- TEM to determine if the reinforcement phases are coherent with the Ti matrix
- Characterization of mechanical properties and corrosion resistance
- Scale-up of SPS to larger lots of materials

Acknowledgement: Dr. Munir, UC Davis