Synthesis of Dense TiC-Ti Cermets via SHS and QIP

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Outline

- Introduction.
- Theoretical modeling.
- Experiments.
- FEM simulations.
- Conclusions.
- Future work.

Introduction of SHS and QIP

Self-propagating High-temperature Synthesis (SHS)



The synthesis of materials/compounds is achieved in wave of chemical reaction/combustion that propagates over starting reactive mixture via layer-by-layer heat transfer

Photo courtesy: http://www.ism.ac.ru/handbook/shsf.htm

SHS Product and Applications

- Composites materials. (TiC+Al₂O₃)
- Materials with specific properties.(BaTiO3)
- Cutting tools and polishing powder. (TiC)
- Shape memory alloys. (TiNi)
- Intermetallic compounds. (Ni Aluminides)
- Thin films and coatings, (TiB₂)
- Heating elements. (MoSi₂)
- Bioengineering implants. (Ti+TiB)

Advantages of SHS

- Volatilizing low boiling point impurities.
- Avoids expensive processing facilities.
- Short operating and processing time and cost.
- Inorganic materials can be synthesized and consolidated into final product in one step.
- Obtain specific phase of the materials.

SHS Problems and Challenges

- Final mechanical and physical properties (excessive porosity).
- Explosive character of SHS.
- Short processing time -- hard to control.
- High temperatures and rapid cooling cause operational difficulty.

Solution: Post-Combustion Densification: QIP (Quasi-Isostatic Pressing).

Different Consolidation Setups



Controlling Parameters of SHS

- Reactants composition.
- Time between combustion and consolidation
- Consolidation load and schematics.
- Particle size and shape.
- Particle preparation and handling.
- Green density of sample.
- Combustion temperature and rate.
- Gravity.

Generic Research Goal

Net-shape fabrication of dense TiC-Ti cermets

Research Route



Research Components

Theoretical Modeling

Analysis of applicability of various models, finding first model approximations for process and material parameters.

• Experiments

Determination of optimal process and material parameters:

Optimal composition of the cermet, optimal composition of the PTM, time scheme of combustion and densification procedure.

• FEM Simulation

Controlling and optimizing the shape change under QIP.

Scientific Novelties

- For the first time, dense TiC-Ti cermets is synthesized by using SHS and QIP technique.
- As first approximation, an elastic model describing the constitutive behavior of PTM is created. The optimal composition of PTM was determined.
- Technical parameters that are critical in the fabrication of dense net-shape final products via SHS and QIP, such as cermet composition, time window between combustion and densification, densification load, particle size, have been investigated.
- A FEM code based on the nonlinear-viscous porous bodies theory developed by Dr. E.A. Olevsky and Dr. A. Maximenko has been further developed to simulate the QIP process.
- Both the constitutive behavior of the TiC-Ti and the PTM have been implemented into commercial FEM package ABAQUS to simulate and optimize the densification process of the TiC-Ti cermet in QIP setup.

Theoretical Modeling

Objective and Tasks

- Understand the constitutive behavior of porous cermets during high-temperature densification.
- 1. Determine the constitutive parameters: shear and bulk moduli for porous materials used in the study.
- 2. Model the porous cermets as a rigid-plastic material and compare the results with experimental results .
- **3.** Model the porous cermets as a power-law creep material and compare the results with experimental results.
- 4. Determine which model of shear and bulk moduli has best agreement with experimental results and whether rigid-plastic models or power-law creep models for porous cermets should be employed

Objective and Tasks (continue I)

• Understand the constitutive behavior of PTM

- 1. Conduct compression experiments of PTMs with different concentrations of fused alumina and graphite.
- 2. Model the compressive constitutive behavior of PTM with respect to porosity of the PTM and composition of fused alumina and graphite in the PTM

Objective and Tasks (continue II)

- Model and optimize the densification process of the porous cermets in QIP setup.
- 1. Determine related materials parameters of the porous cermets needed in the modeling. Conduct after combustion indentation experiments.
- 2. Model the constitutive behavior of the porous cermets in QIP densification mode.
- 3. Determine the optimal PTM concentration in order to obtain netshape final products with a high final density

The Main Constitutive Relationship



externally applied material resistance sintering stresses

Linear Viscous: $\sigma(W) = 2\eta_0 W$ Rigid Plastic: $\sigma(W) = \sigma_y$ Power Law Creep: $\sigma(W) = AW^m$ $W = \frac{1}{\sqrt{1-\theta}} \sqrt{\phi \dot{\gamma} + \psi \dot{e}^2}$

Yield Criterion of Porous Materials

$$\frac{P^2}{\psi} + \frac{\tau^2}{\varphi} = \delta \sigma_{y_0}^2$$

Where *P* is the first invariant of stress tensor, τ is the second invariant of stress tensor deviator. σ_{y0} is the yield stress of the fully dense material. For the case of uniaxial compression of an axisymmetric body, it is assumed that $d\varepsilon_r = d\varepsilon_{\theta} = 0$ and $\sigma_r = \sigma_{\theta} = [v/(1-v)]\sigma_Z$ (where *v* is Poisson's ratio). The stress tensor invariant are then given by:

$$P = \frac{\sigma_r + \sigma_\theta + \sigma_z}{3} = \frac{1}{3} \left(\frac{1 + v}{1 - v} \right) \sigma_z$$

$$\tau = \sqrt{\frac{1}{3} \left[\left(\sigma_r - \sigma_\theta \right)^2 + \left(\sigma_\theta - \sigma_z \right)^2 + \left(\sigma_z - \sigma_r \right)^2 \right]} = \sqrt{\frac{2}{3}} \left(\frac{1 - 2v}{1 - v} \right) \sigma_z$$

Different Models for Constitutive Parameters of Porous Materials

φ	Ψ	δ	
$\frac{1}{\rho^2}$	$\frac{3}{2}\frac{(1-\rho)}{\rho^3}$	ρ	-
$\frac{3}{2}\rho\left(2+\rho^2\right)$	$\frac{9}{2}\rho(3-\rho)(1-\rho)$	ρ	
$\frac{9}{2} \frac{1 - (1 - \rho)^2}{1 + (1 - \rho)^3}$	$\frac{9}{2} \frac{(1-\rho)^2 \left(1-(1-\rho)^2\right)}{1+(1-\rho)^3}$	ρ	
$\frac{3(2+\rho^2)}{2(2\rho^2-1)}$	$\frac{9(3-\rho)(1-\rho)}{2(2\rho^2-1)}$	1	
$\left(\frac{\rho}{2-\rho}\right)^{\frac{2}{m+1}}$	$\frac{2}{3} \left(\frac{1 - (1 - \rho)^m}{m(1 - \rho)^m} \right)^{\frac{2}{m+1}}$	ρ	
	φ $\frac{1}{\rho^2}$ $\frac{3}{2}\rho(2+\rho^2)$ $\frac{9}{2}\frac{1-(1-\rho)^2}{1+(1-\rho)^3}$ $\frac{3(2+\rho^2)}{2(2\rho^2-1)}$ $\left(\frac{\rho}{2-\rho}\right)^{\frac{2}{m+1}}$	$\varphi \qquad \qquad$	$\varphi \qquad \qquad$

Where m and ρ are strain sensitive factor and relative density respectively

Stress-Density Relationship for Rigid-Plastic Models

Doraivelu:

$$\sigma_{Z}(\rho,T) = -\sigma_{y_{0}}\left(1 - \frac{T - T_{0}}{T_{am} - T_{0}}\right)\left(\frac{\rho^{2} - \rho_{i}^{2}}{1 - \rho_{i}^{2}}\right)^{\frac{1}{2}}\left[\frac{\left(2 - \rho^{2}\right)}{\left(1 - \rho^{2}\right)\left(2 + \rho^{2}\right)}\right]^{\frac{1}{2}}$$



Kuhn&Downey:

$$\sigma_{Z} = -\frac{\sqrt{2}}{3}\sigma_{y_{0}}\left(1 - \frac{T - T_{0}}{T_{am} - T_{0}}\right)\left(\frac{2}{2 + \rho^{2}} + \frac{1}{(1 - \rho)(3 - \rho)}\right)^{\frac{1}{2}}$$

Skorohod:

$$\sigma_{z} = -\sqrt{\frac{2}{3}}\sigma_{y_{0}} \left(1 - \frac{T - T_{0}}{T_{am} - T_{0}}\right) \left(\frac{\rho^{\frac{3}{2}}}{\left(1 - \rho\right)^{\frac{1}{2}}}\right)$$

Gurson:

$$\sigma_{Z} = -\frac{\sqrt{2}}{3}\sigma_{y_{0}}\frac{1}{1-\rho}\left(1-\frac{T-T_{0}}{T_{am}-T_{0}}\right)\left[\left(\rho+\left(1-\rho\right)^{2}\right)\frac{2\left(1-\rho\right)^{2}+1}{3}\right]^{\frac{1}{2}}$$

Where $T_0 = 25$ °C is the room temperature, $T_{am} = 2080$ °C which is the liquid phase temperature for alumina. ρ is the relative density.

Comparison of the constitutive models for axial strain compression of hot porous materials and the corresponding experimental curve.



Comparison of the constitutive models for axial strain compression of hot porous materials and the corresponding experimental curve.



Indentation for Determination of A and m





Indentation for Determination of A and m



Indentation for Determination of A and m

Inc: O Time: O.(000e+000	MSCX	
1.000			
0.900			
0.700			
0.600			$A=110MPa \cdot s^{0.2}$
0.500			
0.400			<i>m</i> =0.2
0.300			
0.200			
0.100			
0.000			
	job1		
	Displacement	1	

Stress-Density Relationship for Power Law creep Models

Gurson:

$$\sigma_{z}(\rho,T) = -A\left(1 - \frac{T - T_{0}}{T_{am} - T_{0}}\right) \frac{\left[\frac{4}{27} \frac{\left(1 + (1 - \rho)^{3}\right)}{\left(1 - (1 - \rho)^{2}\right)^{2}} + \frac{2}{9} \frac{\left(1 + (1 - \rho)^{3}\right)}{\left(1 - (1 - \rho)^{2}\right)\left(1 - \rho\right)^{2}}\right]^{\frac{m+1}{2}}{\rho^{\frac{m-1}{2}}} \dot{\varepsilon}_{z}^{m}$$



Skorohod:

$$\sigma_{Z}(\rho, T) = -A\left(1 - \frac{T - T_{0}}{T_{am} - T_{0}}\right) \rho^{\frac{m+3}{2}} \left[\frac{2}{3} + \frac{2}{3}\frac{\rho}{(1 - \rho)}\right]^{\frac{m+1}{2}} \dot{\epsilon}_{Z}^{n}$$

Kuhn&Downey:

$$\sigma_{Z}(\rho, T) = -A\left(1 - \frac{T - T_{0}}{T_{am} - T_{0}}\right) \frac{\left[\frac{4}{9\rho(2 + \rho^{2})} + \frac{2}{9\rho(1 - \rho)(3 - \rho)}\right]^{\frac{m+1}{2}}}{\rho^{\frac{m-1}{2}}} \dot{\varepsilon}_{Z}^{m}$$

McMeeking & Sofronis:

$$\sigma_{Z}(\rho,T) = -A\left(1 - \frac{T - T_{0}}{T_{am} - T_{0}}\right) \frac{\left[\frac{2}{3}\left(\frac{\rho}{2 - \rho}\right)^{\frac{2}{m+1}} + \frac{2}{3}\left(\frac{1 - (1 - \rho)^{m}}{m(1 - \rho)^{m}}\right)^{\frac{2}{m+1}}\right]^{\frac{m+1}{2}}}{\rho^{\frac{m-1}{2}}} \dot{\epsilon}_{Z}^{m}$$

Where m is the stain rate sensitivity. A plays the role of a yield stress of a fully-dense material as in Rigid-Plastic models

Comparison of the constitutive models for axial strain compression of hot porous materials and the corresponding experimental curve.



Comparison of the constitutive model for axial strain compression of hot porous TiB_2 -Al₂0₃ and the corresponding experimental curve.



Conclusions on Cermets High Temperature Constitutive Behavior

The best model to use is power-law creep with Skorohod viscosity moduli.

$$\varphi = \frac{1}{\rho^2}$$
$$\psi = \frac{3}{2} \frac{(1-\rho)}{\rho^3}$$

Cracking of Graphite Particles in PTM



Compression Test of PTM



Elastic modeling of PTM



First approximation and possible analytical optimization.

$$E(C, \rho) = E_C \cdot E_{\rho_p}$$
$$E_C = 95.7854 \cdot (C+1)^{-0.27281}$$
$$E_{\rho_p} = (0.0118 \cdot \rho_p - 0.1794)$$



Modeling of QIP

Based on the fact that:

$$\sigma_{ZP} = \sigma_{ZZ}$$

And the constitutive modeling of PTM as well as our former study one have:

$$\frac{d\theta}{d\tau} = -(1-\theta) \left[\frac{143.68}{E_0} (C+1)^{(-0.27281)} (0.0118(1-\theta_p) - 0.1794) \right]^{\overline{m}} \times \left[\frac{(4-3\theta_p)}{9\theta_p (1-\theta_p)} \ln \left(\frac{1-\theta_p}{1-\theta_{p_0}} \right) \frac{(2-\theta_p)}{(2-3\theta_p)} \frac{\theta}{(1-\theta)^3} \right]^{\overline{m}} \left[\frac{\sqrt{6}(1-\theta)\sqrt{\theta_p^2 (1-\theta) + \theta(1-\theta_p)^2}}{\theta(4-3\theta_p)} \right]^{1-m}$$

 $au = \left(\frac{A}{E_0}\right)^{\frac{1}{m}} t$ Normalized time (t is physical time)



Modeling of QIP (continue I)

From the geometry relationships:

$$\frac{d\left(H/H_{0}\right)}{d\tau} = \frac{H}{3H_{0}} \left[\frac{2\theta_{P} + (1 - 3\theta_{P})\theta}{\theta(1 - \theta)(1 - \theta_{P})} \right] \frac{d\theta}{d\tau}$$
$$\frac{d\left(R/R_{0}\right)}{d\tau} = \frac{R}{3R_{0}} \left[\frac{\theta - \theta_{P}}{\theta(1 - \theta)(1 - \theta_{P})} \right] \frac{d\theta}{d\tau}$$


Modeling of QIP (continue II)

From conservation of mass of the system of PTM + porous cermets:



$$\frac{d\left(\theta_{P}/\theta_{P_{0}}\right)}{d\tau} = \frac{\left\{\frac{\rho_{Spe}}{\rho_{PTM}}\left[2\frac{R}{R_{0}}\frac{H}{H_{0}}\frac{d\left(R/R_{0}\right)}{d\tau}(1-\theta) + \left(\frac{R}{R_{0}}\right)^{2}\frac{d\left(H/H_{0}\right)}{d\tau}(1-\theta) - \left(\frac{R}{R_{0}}\right)^{2}\frac{H}{H_{0}}\frac{d\theta}{d\tau}\right]\right\}}{-\left[\left(\frac{R_{d}^{0}}{R_{0}}\right)^{2}\frac{\dot{\theta}}{H_{0}}\left(\frac{A}{E_{0}}\right)^{\frac{1}{m}} + 2\frac{R}{R_{0}}\frac{H}{H_{0}}\frac{d\left(R/R_{0}\right)}{d\tau} + \left(\frac{R}{R_{0}}\right)^{2}\frac{d\left(H/H_{0}\right)}{d\tau}\right](1-\theta_{P})\right]}{\left[\left(\frac{R_{d}^{0}}{R_{0}}\right)^{2}\left[\frac{H_{d}^{0} - \dot{\theta}\left(\frac{A/E_{0}}{R_{0}}\right)^{\frac{1}{m}}\tau}{H_{0}}\right] - \left(\frac{R}{R_{0}}\right)^{2}\frac{H}{H_{0}}\frac{d\theta}{d\tau}\right]}\right]$$

A sample kinetics of densification, shrinkage and distortion



Densification and Distortion Rates



Experiments

Objective and Tasks

- Determine the "optimal" nonstoichiometric ratio of Ti and C powders for the synthesis of TiC-Ti cermet
- Understand mechanical and morphological properties of elemental titanium and graphite powders used in this study.
- Conduct a series of combustion experiments without densification for different nonstoichiometric ratios of titanium and graphite powders.
- 3. Determine the optimal nonstoichiometric ratio to be used in further studies.

Objective and Tasks (continue)

- Determine the time window between combustion and densification and the densification load needed to obtain dense net-shape final products
 - 1. Determine the time window between combustion and consolidation in order to obtain dense net-shape final products.
 - 2. Determine the load needed to obtain dense net-shape final products.
 - 3. Compare the experimental results on shape distortion with theoretical modeling results and make necessary adjustments to the theoretical models.

Elemental Ti and C Powders





Ti Powder



Ti + C Mixture



Best Nonstoichiometric Ratio



Time Window



Parameters	Time Zone	Times(s)
Delay	t1	4-5
Loading Time	(t2-t1)	5-10
Holding Time	(t3-t2)	10-15
Unloading Time	(t4-t3)	1-2

Time Window (continue)



Radial cracks caused by excessive delay



Less ductility results in high porosity

Load Scale



Load is not a critical factor. Based on experiments and former studies, a densification load between 50 Tons and 70 Tons is used for further investigation.

Other Factors

• Influence of C particle size: Small Size -> Excessively Active



• Influence of low melting temperature metallic binder

Final Product



Finite Element Method Simulation

FEM Simulation Objective and Tasks

- FEM method to simulate densification of porous materials in QIP setup and optimize initial shape of green sample to get net-shape final products.
- Determine material parameters needed to conduct FEM simulation (A, m, Initial Porosity).
- 2. Develop an FEM simulation of QIP based on the theory of nonlinearviscous porous bodies (by E.A. Olevsky and A. Maximenko).
- 3. Conduct FEM simulation of QIP using Mohr-Coulomb and Drucker-Prager models of the commercial FEM package ABAQUS for PTM.
- 4. Optimize initial shape of a green sample in order to obtain highdensity net-shape final products of SHS-QIP technological sequence.

Theory of Plastic Porous Materials

If energy dissipation in the material depends only on the strain rate tensor components: (*D* is average dissipation rate density)

$$\Phi = \int_{0}^{1} D(\alpha \dot{e}, \alpha \dot{\gamma}) \frac{d\alpha}{\alpha}$$

The dissipation potential is the main component in the extremum principle for the kinematic parameters of deformation. It was proved that velocities of a real deformation process render the minimum for the following functional:

$$I = \int_{\Omega} \Phi d\Omega - \int_{\Omega} F \cdot v d\Omega - \int_{S} T \Box v dS$$

In minimization of *I*, the following approximation of *D* was used in iterative method of viscous approximations

$$D \approx D_{v} = \sigma_{0} \dot{\varepsilon}_{0}^{-m} \sqrt{1 - \theta} \frac{\psi \dot{e}^{2} + \varphi \dot{\gamma}^{2}}{(\psi \dot{e}_{0}^{2} + \varphi \dot{\gamma}_{0}^{2})^{\frac{1 - m}{2}}}$$

Schematic Representation of QIP Setup



Finite Element Model



Mesh and Boundary conditions

Finite Element Model (continue I)



Material properties

Finite Element Model (continue II)



Initial conditions

FEM Results (Nonlinear-Viscous Porous Theory)

Inc: 0 Time: 0.000e+000		MSC	
0.500			
0.475			
0.450			
0.425			
0.400			
0.375			
0.325			
0.300			
0.275			
0.250			
0.225			
0.200			
0.150			
0.125			
0.100			
0.075			
0.050			
0.025	х [°]		
0.000			
	Perceitu	~	
	Porosity	4	

Determination of q₁,q₂ **and** q₃ **for Tvergaard-Gurson Model**

FEM Results (Mohr-Coulomb Model)

FEM Results (Drucker-Prager/Cap Model)

FEM Results (Drucker-Prager/Cap 3D Model)

Comparison of the Results of the Three Models

Comparison of Distortion Aspect Ratio

Optimization of Initial Shape

Optimization of Initial Shape

Conclusions

Conclusion (Theoretical Modeling)

- 1. Modeling of pressing of porous materials in a rigid die shows that the Skorohod model for bulk modulus and shear modulus and power law creep material constitutive behavior of the material have the best agreement with the experimental results.
- 2. As a first approximation, PTM can be modeled as an elastic material. The elastic constitutive behavior of the PTM can be modeled as a function of composition of fused alumina and graphite in the PTM and the porosity of the PTM.
- 3. Densification and distortion of the porous combustion reacted material were successfully modeled. An optimal composition of 75%wt. fused alumina and 25%wt. graphite was chosen for the purpose of QIP applications in further studies.

Conclusion (Experiments)

- 1. A mole composition between Ti:C = 1.4:1.0 and Ti:C = 1.6:1.0 gives the best final product from the viewpoint of morphology and mechanical properties. For the purpose of obtaining a high hardness final product, the mole ratio of Ti:C = 1.4:1.0 is used in further investigations.
- 2. Based on the experiments and former study results, a consolidation load of 50 to 70 tons is found to be the proper load in order to obtain dense final products.
- 3. A time window less than 5 seconds between combustion and consolidation is proposed. A preload combustion system is designed for this purpose.
- 4. Small size C particles result in more intensive reaction and more cracks in final products.
- 5. A low melting temperature metallic binder helps decreasing cracks and improving mechanical properties of final products.

Conclusion (FEM Simulation)

- 1. A finite element model, where the porous combustion reacted material was modeled as a power law creep material and the PTM was modeled as a rigid-plastic granular material, was created. The simulation results show similar deformation and distortion of the combustion reacted material to experiment results.
- 2. Both the Mohr-Coulomb and Drucker-Prager/Cap models are used for modeling of constitutive behavior of PTM with acceptable agreement of experimental results.
- 3. An optimized initial shape for obtaining of a net-shape final product is obtained

Published/Submitted Papers

- J. Ma, E.A. Olevsky, and M.A. Meyers, Modeling of Densification of Porous and Ductile Cermet Composites, Proc. 2001 NSF Design, Service & Manufacturing Grantees & Research Conference (EPP CD-ROM Proceedings), 8p., Tampa, Florida (2001).
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- 2nd Place Award, 16th Annual CSU Student Research Competition Engineering Group (2002).
- E.A. Olevsky, J.C. LaSalvia, J. Ma, and M.A. Meyers, Densification of Porous Bodies in a Granular Pressure-Transmitting Medium: Part I, Shrinkage Anisotropy, Submitted to Acta Materialia (2004).
- E.A. Olevsky, J.C. LaSalvia, J. Ma, and M.A. Meyers, Densification of Porous Bodies in a Granular Pressure-Transmitting Medium: Part II, Shape Distortion, Submitted to Acta Materialia (2004).

Suggested Future Works

- 1. Analysis of the thermodynamics of combustion synthesis: solution of a coupled heat transfer densification problem.
- 2. Applications to nano-materials (recently reported by Z.A. Munir *et al.* grain size retention during SHS).
- 3. Solution of inverse problems of QIP to obtain the desired final complex net-shape products.
- 4. Fabrication of functionally graded composite combustionsynthesized cermets.

Questions?